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## FIFTY YEARS OF ELECTRONS

by W. de GROOT.

537.122:537.533

In the publication "On Cathode Rays" by J. J. Thomson (Oct. 1879) the existence of free electrons was first irrefutably established. This important article, which appeared just 50 years ago, is discussed in detail. A short account is then given of the investigations which preceded Thomson's publication and of the results of the further theoretical study of electrons. In conclusion a survey is given of a number of technical applications in the field of "electronics".

### Introduction

We can assign no more suitable date to the discovery of the electron than the date of publication, October 1897, of J. J. Thomson's paper "On Cathode Rays"<sup>1</sup>). The object of Thomson's investigations was to acquire more knowledge about the nature of cathode rays, about which at that time the most divergent opinions were held.

Some people considered these rays to be charged "particles", others denied their corpuscular nature and were of the opinion that it was mainly a question of a phenomenon in the "ether".

Thomson remarked that an explanation which starts from the corpuscular nature as a working hypothesis is more likely to be successful and can more easily be tested by known laws (namely those of mechanics) than an explanation on the basis of an hypothesis about the ether, because the properties of the "ether" itself are too little known to base conclusions upon them.

The experiments described were thus devised "to test some of the consequences of the electrified-particle theory".

### Thomson's deflection experiments

The objects of Thomson's experiments were:

a) to verify that the cathode rays carry a charge

and that this charge accompanies the rays when they are deflected by a magnetic field;

b) to investigate quantitatively the qualitatively known deflection in an electric field, which also indicates the presence of a charge;

c) to measure the energy of the rays and, by a combination of this measurement with that of the magnetic deflection, to determine the velocity and the ratio of charge to mass;

d) to determine the same quantities by a combination of the magnetic and electric deflections.

In all these experiments the cathode rays were obtained by a discharge in a tube filled with a rarefied gas, in which electrodes were fused or cemented in. An induction coil or a galvanic battery served as source of voltage.

The experiment *sub a*), an improved version of an experiment by Perrin<sup>2</sup>), was performed with the tube of *fig. 1*. Cathode rays leave the cathode *K* and through an opening in the anode *A* reach the space *R*, where they are deflected by a magnetic field and, through an opening in an earthed cylinder *B*, reach a second conductor *D* mounted inside that cylinder. An increase in the charge, registered by an electrometer connected with *D*, is only shown when the rays strike the opening. This proves that a charge is indivisibly connected with the cathode rays. The charge is a negative one.

<sup>1</sup>) J. J. Thomson, On Cathode Rays, Phil. Mag. 44, 293-316, 1897 (October, article dated Aug. 7, 1897). Some of the experiments described in this article had already been published elsewhere by Thomson (Proc. Cambr. 9, 1897) and demonstrated (Royal Institution, Friday evening lecture Apr. 30, 1897, see Electrician, May 21, 1897).

<sup>2</sup>) In Perrin's experiment a Faraday cage was placed directly opposite the cathode, when it was found that no charge was conducted to the cage when the cathode rays were deflected by a magnet.



The magnetic deflection was further investigated quantitatively by means of the tube of *fig. 2*, which is nothing else but an air-pump bell jar fitted with electrodes. It is found that the rays are not all

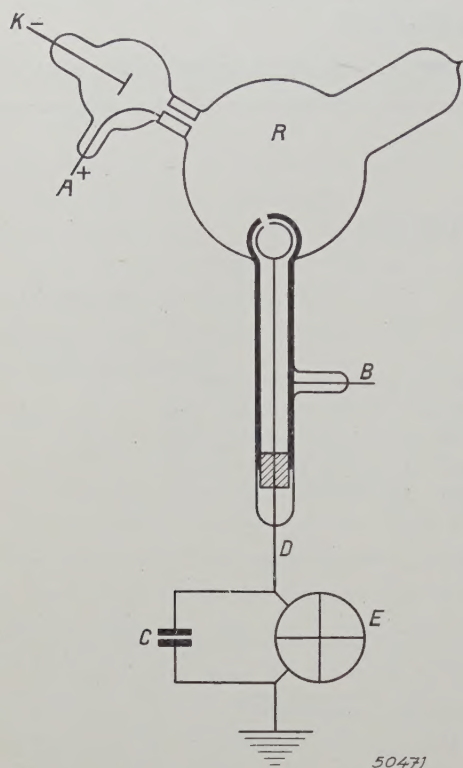


Fig. 1. Discharge tube according to J. J. Thomson, with which the (negative) charge of magnetically deflected cathode rays was demonstrated. *K* cathode, *A* anode, *B* earthed cylinder, *D* electrode for capturing the cathode rays, *E* electrometer, *C* condenser. The magnetic field is excited in the space *R* by wire coils placed outside the tube.

equally deflected (magnetic spectrum) and that the components making up the largest part of the beam, causing a strong fluorescence of the glass wall, are not the same as those which cause the strongest luminescence of the gas. The most striking characteristic observed in this tube, however, was that, with a given voltage between anode and cathode, the appearance of the deflected beam is always the same whatever the nature of the gas filling.

The deflection *sub b*) by an electric field was investigated in the tube of *fig. 3*, the precursor of our modern cathode-ray oscillograph.

Experiment *c*) was performed in a similar tube but without deflection plates and provided with a screened electrode (as in *fig. 1*). The innermost insulated electrode contained a thermo-element which was struck by the cathode rays and whose increase in temperature during a given time was measured. At the same time, with the aid of a quadrant electrometer, the charge taken up by the element was measured.

If, in the time *t*, *N* particles strike the thermo-element, each bearing a charge *e*, the total charge is

$$Q = Ne \dots \dots \dots (1)$$

From the temperature increase the total energy *W* is also known:

$$W = N \cdot \frac{1}{2} mv^2, \dots \dots \dots (2)$$

where *m* represents the mass and *v* the velocity of the particle.

Finally the radius *r* was measured of the orbit described by the particles in a field *H*<sup>3)</sup>.

$$\frac{mv^2}{r} = e v H \dots \dots \dots (3)$$

When *rH* = *I* it follows from (1), (2) and (3) that

$$v = \frac{mv^2}{erH} = \frac{Nmv^2}{NerH} = \frac{2W}{QI} \quad \text{and} \quad \frac{m}{e} = \frac{rH}{v} = \frac{QI^2}{2W}.$$

In this way the following results were obtained in tubes with different gas fillings.

	air	H <sub>2</sub>	CO <sub>2</sub>
$\frac{m}{e}$	0.44	0.47	$0.45 \cdot 10^{-7}$ g/emu
$\frac{v}{v}$	0.28	ex 1.2 · 10 <sup>10</sup> cm/sec	

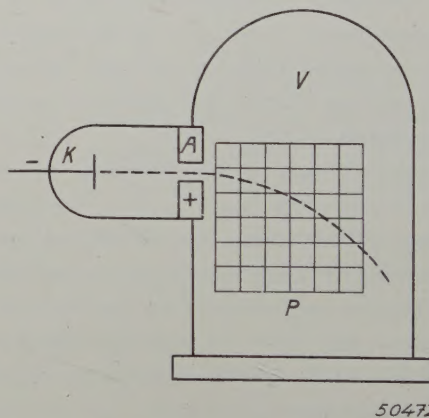


Fig. 2. Discharge vessel in which the magnetic deflection was investigated by Thomson. The rays from the cathode *K* pass through an opening in the anode *A* into the bell jar *V*. The curvature in a magnetic field (excited by coils of wire placed outside the vessel) is measured by causing the rays to pass along a glass plate *P*, upon which there is a network of lines which is photographed together with the cathode rays.

The deflection experiments *sub d*) are based on the measurement of the changes in direction taken by the ray in an electric or magnetic field. If *F* is

<sup>3)</sup> It would be better to write *evB*. In electromagnetic units as used by Thomson, however, *B* = *H*.



the electrical field strength the lateral acceleration is  $Fe/m$  and the lateral velocity after travelling a distance  $l$  between the plates is  $(Fe/m) l/v$ , so that the following holds for the angle of deflection  $\vartheta$ :

$$\vartheta = \frac{Fel}{mv^2}.$$

The deflection in the case of a magnetic field is  $\varphi = l'/r$ , where  $l'$  represents the distance travelled in the field, so that

$$\varphi = \frac{He l'}{mv}.$$

The magnetic field was generated by two coils whose diameter  $l'$  was equal to the length  $l$  of the plates

( $e/m = 1.76 \times 10^7$  e.m.u./g =  $1.76 \times 10^8$  coul./g.). Thomson was at first at a loss to interpret the value found for  $m/e$ . For certain reasons he was of the opinion that the value of  $e$  for the "corpuscles" was many times larger than the charge of a monovalent electrolytic ion. He realized that the corpuscles formed an important component of matter and assumed that each of the atoms contained a large number of these components, the larger the higher the atomic weight. The phenomenon of electric polarization giving rise to a dielectric constant (specific inductive capacity) differing from unity was considered by Thomson to be connected with the corpuscles.

Thomson's publication ends with a discussion

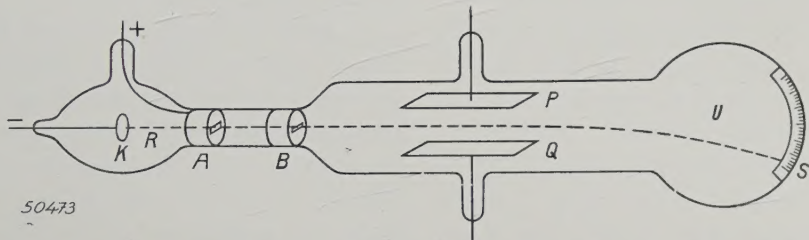


Fig. 3. Thomson's tube for the study of the electrical deflection. The cathode rays formed in the space  $R$  pass through the openings in the electrodes  $A$  and  $B$ . Thus a narrow beam reaches the space  $M$  containing a pair of plates  $PQ$ .  $Q$  is given a positive and  $P$  a negative potential with respect to  $B$ . The ray is deflected in the electric field between  $P$  and  $Q$  and the deflection is observed by the displacement of the spot of fluorescence on the glass wall at  $S$ .  $S$  is a paper scale on which the displacement is read off.

in the electric deflection experiment. Therefore  $l'$  may be taken equal to  $l$  and one then finds that

$$v = \frac{\varphi}{\vartheta} \frac{F}{H}$$

and

$$\frac{m}{e} = \frac{\vartheta}{\varphi^2} \frac{H^2}{F} l.$$

These experiments gave the following results:

	air	H <sub>2</sub>	CO <sub>2</sub>
$m/e$	0.12	0.15	$0.15 \cdot 10^{-7}$ g/emu
$v$	0.22	ex 0.36	$\cdot 10^{10}$ cm/sec

The differences in the values of  $m/e$  obtained by the two methods must be ascribed to systematic errors. The agreement between the values obtained by the same method with different gases indicates that the cathode-ray particles are independent of the nature of the gas. The value of  $m/e$  at present accepted as the correct one is  $0.5658 \times 10^{-7}$  g/e.m.u.

of the construction of the atom and describes a model of an atom built up from the results of an experiment with floating magnetic needles <sup>4</sup>). By means of Thomson's model the first attempt was made to explain the periodic system.

Previous history

While conceding all honour due to Thomson, we must not forget his predecessors. In 1820 already Faraday studied discharges in rarefied gases. He distinguished two light phenomena: the negative glow at the cathode and the positive column at the anode, separated by the Faraday dark space. Plücker (1859) and Hittorf (1869) studied the phenomena at the cathode at lower gas pressures. Hittorf described cathode rays and their deflection by a magnetic field, while Goldstein (1876) observed the deflection in an electric field. To

<sup>4</sup>) Thomson mentions as author a certain Professor Mayer. The experiment consists in floating a number of short rod magnets held in corks, for instance with the south pole uppermost. They repel each other but are attracted by a strong magnetic north pole placed above the surface of the liquid. Certain configurations are formed according to the number of magnets.



Hittorf's mind the current flowed from the positive to the negative pole. In his opinion the phenomena at the cathode were the final phase of the process of the discharge. It was too much at that time to think of reversing the order and ascribing the phenomena of discharge to negative particles leaving the cathode.

In 1897 Crookes repeated Hittorf's experiments with an improved technique, especially as regards the evacuation. His lecture entitled "Radiating Matter, or the Fourth State of Aggregation" did much to popularize cathode rays, which by then had definitely come to be recognised as having their origin in the cathode.

In 1883 Hertz declared himself to be an adherent of the corpuscular hypothesis and expressed the desirability of combining the magnetic and electric deviations and thus determining the velocity of the cathode-ray particles, while he had already indicated the possibility of determining the charge electrically or magnetically.

In 1887 he discovered the photo-electric effect, the releasing of a negative charge from a metal conductor by irradiation with ultra-violet light, a phenomenon which was further investigated by Hallwachs (1888). In 1892 Hertz found that thin layers of metals allow the passage of cathode rays. Encouraged by Hertz, in 1894 Lenard succeeded in making cathode rays leave the discharge tube through a window and studying them at will in a very high vacuum. In this way he studied the magnetic deflection. In 1895 he investigated the absorption and scattering in thin metal foils. He found those properties to increase with increasing deflection (decreasing velocity) and, where the rays are of constant velocity, to be proportional to the mass passed through, regardless of the nature of the medium. In the same year, 1895, Röntgen discovered X-rays (or Röntgen rays as they are often called, after their discoverer), which are formed when fast electrons strike a wall or a metal conductor.

Simultaneously with the development sketched above, the idea grew that an electric charge in atomic distribution also occurs in matter. Already around 1870 Weber had put forward the hypothesis that conduction in metals takes place by means of discrete charges which move from atom to atom and are also responsible for the "circulating currents of Ampère", thus for magnetism.

In 1873 Maxwell reluctantly gave as his opinion that in order to explain the phenomena of electrolysis it might be necessary to assume an atomic distribution of electricity, and in 1874 Stoney

made an estimation of this elementary charge ( $3 \times 10^{-11}$  esu) on the basis of the data then available<sup>5</sup>). In 1891 Stoney called this charge the electron. Originally the term meant the charge itself and not a definite particle bearing this charge. In this sense the atom contained positive as well as negative "electrons".

Later on the name electron came to be used for the "corpuscles" discovered by Thomson in the cathode rays, which we now call "free electrons" in contrast to the "bound electrons" occurring in atoms.

The hypothesis that the charges in the atom can vibrate about an equilibrium and thus govern the optical properties of matter was proposed by Lorentz (1875), among others, and worked out by him into a theory (1892).

In 1896 Zeeman discovered the magnetic resolution of the spectral lines. Together with Lorentz he decided, from the sign of the circular polarization exhibited by the lines when viewed along the lines of force, that the particles in the atoms responsible for the emission of light carry a negative charge. From the magnitude of the splitting, moreover, he was able to make a rough estimation of the quotient  $e/m$ , which, expressed in emu/g, was found to have the value  $10^7$ , the same value which Thomson shortly afterwards found for the cathode-ray particles<sup>6</sup>). Though Zeeman himself did not at that time venture to draw conclusions from his results, it may be claimed that it was this discovery that lent strength to the idea of "bound" electrons in the atom.

### Further development

We have seen that after the quotient  $m/e$  of the cathode rays had been determined Thomson had some doubts about the charge  $e$  and at first thought it to be much larger than the charge of a monovalent ion. Since 1896 Thomson and Rutherford had been studying the ionization of gases by X-rays. C. T. R. Wilson had found that water vapour can condense on the gaseous ions, a phenomenon which he subsequently utilised to show the paths of ionizing particles in a gas (Wilson Chamber, 1912). From an estimation of the number of water droplets, combined with a determination of the total charge, Thomson (1898) was able to determine the charge of one droplet, which he considered equal to the ion charge. He found it to be of the same order as the charge of electrolytic ions. A

<sup>5</sup>) The value of  $e$  at present accepted as correct is  $4.80 \times 10^{-10}$  esu =  $1.6 \times 10^{-19}$  coulomb.

<sup>6</sup>) Thomson points this out in his lecture (see footnote <sup>1</sup>).



similar result had shortly before been found by Townsend for the charged water droplets formed above the surface of an electrolyte when gas bubbles escape from it upon current being passed through. Wilson (1903) improved upon Thomson's method by studying the effect of a vertical electric field on the rate of settling.

Since in the process of ionization of X-rays a molecule is not divided into two ions, as in electrolytic dissociation, but the atom itself is split into charged components (monatomic gases like argon are also ionized by X-rays), it was concluded that the charge found in the gaseous ions, being of the same order as the ionic charge in electrolysis, was the charge  $e$  of the electron.

Wilson's method was later (1909) worked out in Millikan's laboratory to a precision method for the determination of  $e$ . The accuracy of this method is even now scarcely surpassed by the indirect determination of the electrolytic unit charge, which, as will be known, is derived from the electrochemical equivalent in connection with the determination of Avogadro's number from X-ray interferences in crystals.

From the values of  $e$  ( $1.6 \times 10^{-19}$  coulomb) and  $e/m$  ( $1.76 \times 10^8$  coul/g) it follows that the mass of the electron is  $9.1 \times 10^{-28}$  gram, *i.e.* 1/1873 of the mass of a hydrogen atom.

The discovery of bound electrons led gradually to certain conceptions concerning the structure of the atom. As we have seen, Stoney already assumed that positive and negative charges are present in the atom.

Lenard (1903) imagined these charges as occurring in pairs (dynamids), while Thomson, in view of his experiments with the model described above, assumed that the atom consisted of a sphere homogeneously filled with positive charge, within which, under the influence of the positive attraction and the mutual repulsion, the electrons take up certain equilibrium positions.

To Rutherford (1911) is due the conception that the positive charges in the atom are collected in a positive nucleus, which also carries the larger part of the atomic mass <sup>7)</sup>.

Rutherford, who had been studying radioactive phenomena since 1897, was led to this conclusion by experiments on the scattering of alpha particles by thin metal foils. Rutherford's conception of a positive nucleus surrounded by a swarm of negative electrons formed the basis of Bohr's (1913) model of the atom and his ideas about the

structure of the periodic system, which ideas were supported especially by Moseley's experiments (1912) on the X-ray spectra of atoms.

In 1924 De Broglie predicted theoretically the wave nature of the electron, which was experimentally confirmed in 1927 by the experiments of Davisson, Germer and G. P. Thomson.

In 1925 Uhlenbeck and Goudsmit explained a number of unaccountable phenomena in the spectra by ascribing to the electron the properties of a top. This so-called spin of the electron is in fact the chief source of magnetism.

Finally, in 1932, Anderson discovered the positive electron in cosmic rays, possessing the same ratio  $e/m$  but having a positive charge.

Soon afterwards it was found that also many artificial radio-active isotopes emit positive electrons, forming the counterpart of the negative electronic rays (beta rays) familiar since the first days of radio-activity. The existence and properties of the positive electron were more or less foretold by Dirac. It has the tendency to combine with a negative electron under emission of radiation (annihilation). Conversely, from a quantum of radiation of sufficiently high energy ( $> 1$  Me V) an electron pair (+ and —) can be created.

### The rôle of free electrons in technology

It must not be considered as mere chance that the electron was discovered at a time when important progress was being made in vacuum technique owing to the development of the incandescent electric lamp.

Edison had already discovered that when a third electrode is introduced into the bulb of a carbon filament lamp and connected with the positive end of the filament a negative current passes through the vacuum to that electrode. This thermionic emission of incandescent bodies was carefully investigated by Richardson (1901). The negative particles emitted by a filament are nothing else but free electrons. In this way they can move in an evacuated space without any "gas discharge" being present.

Richardson's experiments led to the invention of the diode as a rectifier and detector of electrical oscillations (Fleming 1904). By the addition of a third electrode or grid, the triode was formed (Lee de Forest 1909), which is the ancestor of radio receiving and transmitting valves in all their various forms. Besides the possibility of generating and detecting electrical waves the radio valve is also of importance as an amplifier of weak A.C. voltages (radio receiving and transmitting installations, line telephony, sound amplification, physical methods of measuring).

<sup>7)</sup> See for example W. de Groot, *Nuclear Physics*, Philips Techn. Rev. 2, 97-102, 1937.



From the diode came the rectifier valves with their various applications (charging of batteries, welding technique, electrolysis).

An important factor in the development of all these applications is the discovery of the electron emission of metal oxides (Wehnelt 1903).

The release of electrons from metals by irradiation with light led to the construction of photocells. In modern photocells use is made of the amplification by secondary electron emission, a phenomenon which is also used in radio valves and which consists in the fact that a surface struck by electrons itself emits electrons.

The cathode-ray tube originated directly from Thomson's experiments; it is used in the form of the cathode-ray oscillograph in technology and in the laboratory to visualize and measure alternating currents and all kinds of phenomena of short duration. From it in turn are derived the applications in radar and television on the one hand, and on the other in the electron microscope.

When a very high voltage is applied between cathode and anode of a discharge tube part of the

energy with which the electrons strike the anode is converted into X-rays. The vacuum X-ray tube with heated cathode (Coolidge 1913) has been developed into a modern apparatus in which voltages of 25 to 2000 kV are employed. These X-ray tubes are used extensively in medical diagnostics and therapy and in the testing of materials.

Finally the study of discharges in rarefied gases, together with the application of the oxide cathode, has led to a number of new light sources (sodium and mercury lamps, fluorescent lamps), which are employed not only for illumination but also for other purposes (ultra-violet irradiation, the analytical lamp).

Thus from the discovery of the electron in the physical laboratory a large number of industrial applications have followed which have been useful in many ways, and which in turn have had a stimulating effect on scientific research. It is not without pride and satisfaction that physicists and technologists may look back upon the accomplishments of the last fifty years, for which so much is due to the work of J. J. Thomson.

See for example W. de Graaf, *Nuclear Physics*, Philips Techn. Rev. 2, 97-102, 1937.

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# EMERGENCY SUPPLY SYSTEMS WITH ACCUMULATOR BATTERIES

by H. A. W. KLINKHAMER.

621.316.261

Emergency supply systems are for serving electric mains-fed plant, such as telephone or lighting installations, in the event of a breakdown in the mains supply. A very suitable system is one where the plant is fed from a rectifier with a battery of lead-cell accumulators connected to it in parallel. The rectifier has to be of such a construction as to ensure a constant output voltage practically independent of mains voltage fluctuations and variations of load. This is necessary to maintain a permanent charge of 2.1 / 2.2 V per cell in the battery, which modern experience proves to be the condition ensuring the longest life for a battery. A rectifier answering these requirements is therefore called a "preserving rectifier". This article explains the advantages of such an emergency supply system compared with a dynamo and the obsolete two-battery system (with two batteries feeding the plant alternately). Finally it is shown that a type of rectifier already described in this journal, with a highly saturated transformer, is quite suitable as a "preserving rectifier", two special applications of which for emergency supply systems are described.

Electricity mains are nowadays the most commonly used source of power for all sorts of plant and installations. The advantages are sufficiently well known. This source of power, however, has one drawback, or perhaps it is better to say that it has a drawback in common with almost all other sources of energy, in that it is liable to a breakdown. Though for many plants and, for instance, for domestic supplies this may not constitute any serious objection provided the interruptions are not too frequent or of too long a duration, there are cases where an interruption in the working of the plant for more than a few seconds — or even not that short — cannot be allowed. To give a striking example, under no conditions may the illumination of an operating table in a hospital fail while an operation is being performed, for that would jeopardize the life of the patient <sup>1)</sup>. Less fatal but equally intolerable is the failure of the lighting in subways, roadtraffic tunnels, cinemas or halls, where a panic is likely to be caused or a situation may arise favourable for pick-pockets. Another important case is that of the telephone, for the slightest interruption in the power supply may have very serious consequences, resulting, for instance, in the mutilation of a telex message that is just being transmitted.

Where in such and similar cases it is desired to keep the plant going in the event of a breakdown in the mains one must have an emergency supply system immediately available. As such there are to be considered in the first place a dy-

namo driven by a combustion engine or else a battery of lead-cell accumulators <sup>2)</sup>.

Here we will deal with supply systems employing accumulator batteries. These possess several obvious advantages, such as simplicity of the installations, noiseless working and the fact that they can be started up without any delay. To judge properly the value of the last mentioned advantage let us consider the steps taken in the case of some P.T.T. plants working with dynamos in order to avoid interruption in the event of a failure of the mains. To bridge over the starting time of the combustion engine, which may be a matter of 30 seconds or so, a compressed air engine is mounted on the dynamo shaft and starts running immediately the mains power fails. Still it would take a few seconds, however, before the dynamo gets up speed, and therefore, to avoid even such a short interruption, a small electro-motor is also set up which keeps the dynamo turning (without load) during normal working, whilst the inertia of a coupled flywheel helps to bridge over the starting period of the compressed air engine. Finally a compressor is needed to recharge the compressed air cylinder after an interruption in the mains supply. There is no denying that a battery system is much simpler.

Nevertheless, designers of power supply systems often show an aversion to the battery solution. From what follows it will be realized, we hope, that this aversion is unwarranted, provided one applies the developments of the last decade in working with batteries. The advantages of the emergency supply system with battery to be described here are such as to merit its application

<sup>1)</sup> This is so important that a safeguard has to be provided not only against interruptions of the mains supply but also against fusing of the incandescent lamp filament. Special lamps have been developed incorporating a reserve filament that comes into action automatically.

<sup>2)</sup> We will disregard here the nickel-iron storage batteries that are used in some cases.



on a much wider scale, both to replace dynamo units and to be installed in cases where hitherto one has had to manage without an emergency supply system on account of the complications involved.

### Hygienics of the lead-cell battery

The aversion to an accumulator battery is due to the idea that it necessarily involves heavy expenditure, a great deal of upkeep and considerable attention. As regards upkeep and attention, it is true that a battery cannot just be stored away in a corner somewhere, as a sort of can of preserved electrical energy, to be used only in case of need. Until fairly recently it was the common belief that, in order to keep a battery in tip-top condition and to make sure that it lasts as long as possible, it must be used; unless it is periodically discharged and fully recharged the plates deteriorate through sulphation ("hardening") and thus reduce the capacity of the battery.

For a number of years already this idea has been refuted by carefully checked practical experience over a great length of time,<sup>3)</sup> and it is now known that a lead-cell battery lasts longest when used in an entirely different way, being kept under what is called a preservation charge. Before proceeding to explain what this means we would point out that the method that used to be commonly practised with batteries for emergency supply systems was based on the obsolete idea mentioned above. The plant was connected to a battery instead of the mains, with a second battery being charged from the a.c. mains *via* a rectifier while the plant was being run off the first one, so that as soon as the first battery was discharged its function was taken over by the second one, and so on alternately. This was the so-called two-battery system, as illustrated diagrammatically in *fig. 1*. It is relatively expensive, because two batteries have to be maintained, while, in a manner of speaking, at any moment one has available as reserve only the power capacity of one battery. It calls for a great deal of maintenance and attention, for the acid strength and meter readings have to be repeatedly checked to see whether it is not time to change over the batteries. If this should be forgotten only once then accidents will happen.

The prejudice that arose against batteries as a medium for emergency supply is thus understandable.

Against the old battery treatment we now have a new method, that of keeping the battery charged continuously with a low charging current, just sufficient to compensate the internal losses. This is done by maintaining a permanent voltage of 2.1 / 2.2. V per cell on the battery.

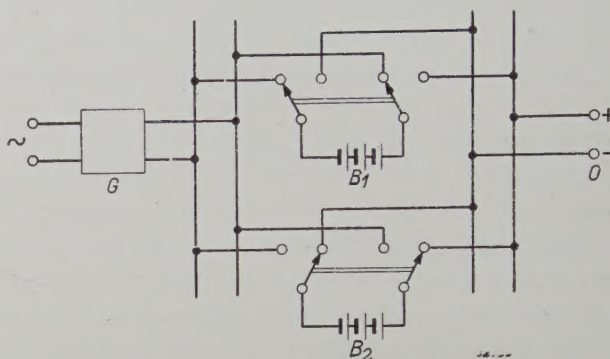


Fig. 1. Two-battery system. While the battery  $B_2$  is feeding the plant connected at  $O$  the battery  $B_1$  is being charged by the rectifier  $G$ . When battery  $B_2$  becomes exhausted two switches are thrown over and the functioning of the batteries is interchanged until  $B_1$  is exhausted, and so on.

The fact that under these working conditions the battery will last longest may be made clear from the following somewhat simplified considerations. In the process of discharging sulphate of lead is formed in a fine crystalline structure, and after a time, about a week, this begins to change into a coarse crystalline formation. This is the phenomenon of the "hardening" of the plates already mentioned. Provided not too long a time is allowed to elapse the sulphate of lead can, it is true, be reduced again to a fine crystalline structure by repeated deep discharging followed by overcharging, but then it is inevitable that in the overcharging of the battery it will "boil" or "gas" for quite a time, and this "gasing" is most harmful for the life of the battery. It destroys mechanically the skin of  $PbO_2$  right down in the depth of the pores, thus reducing the active surface. Later on a fresh skin of  $PbO_2$  is formed on the exposed lead, thereby increasing again the active surface. Every time this takes place, however, the acid burns deeper and deeper into the metal, causing the plate to become spongy and shortening its life. Now, neither of these two causes of ageing — hardening through discharge and becoming spongy through the gasing — occur when a battery is kept under a preservation charge, because then it does not lose any charge and does not gas.

<sup>3)</sup> See, *i.a.*, E. Anderfuhren. *Techn. Mitt. Schweiz T.T.* 19, 146-151, 1941; H. Grau, *Die Stromversorgung von Fernsprechwähleranlagen*, Verl. R. Oldenburg 1943, page 14; also U. Lamm *ASEA J.* 20, 3-9, 1947 (No. 1), in which article the line of thought followed is similar to that here.



It may be said, therefore, that a battery (not subjected to shocks) permanently kept to a cell voltage of 2.1 — 2.2 V has practically eternal life, whereas if it is left to perform its natural function of giving off and taking up charges a battery must inevitably age.

### Single-battery system versus two-battery system

In practice the method of preservation charging for an emergency supply system could be applied according to the diagram in *fig. 2*. It is assumed

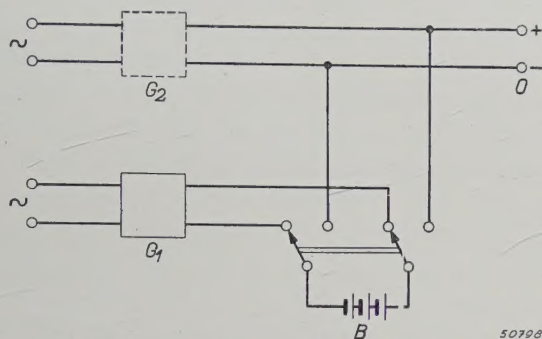


Fig. 2. Emergency supply system with only one battery and two rectifiers. While the plant connected at *O* is being fed from the rectifier  $G_2$  (sometimes direct supply from the mains is also possible) the battery *B* is being kept under a preserving charge from its own rectifier  $G_1$ . In the event of the mains failing *B* is switched over to the plant.

that the plant is fed from the a.c. mains *via* a rectifier. If the plant can be run equally well on a.c. or d.c. voltage this rectifier can be dispensed with. There is only one battery, permanently connected to its own rectifier, which must be capable of keeping the battery up to a preservation charge or charging it properly after a discharge. In the event of the mains failing the battery is then switched over, maybe automatically, from its charger to the plant, and when the mains voltage comes on again it is switched back to the rectifier.

A still simpler circuit is to connect the plant and the battery in parallel to the same rectifier. This system, which is the most important from a practical point of view, is represented in *fig. 3*. In case of a mains breakdown the permanently connected battery takes over the feeding of the plant without any switching and without any interruption.

A "single battery system" as outlined here has important advantages over the two-battery system previously described.

In the first place the full capacity of the battery is always available for keeping the plant running in case of need. For a certain duration of "reserve running" roughly only half the battery capacity is required for a single-battery system compared with the two-battery system, thus halving the

initial cost and the space required. Furthermore, one can then dispense with the switchboard with bus-bars, switches, separate mains switch, voltmeter and ammeter for each battery.

A second advantage is one of efficiency. In a two-battery system every kWh of the power output is first accumulated in the battery, which is not the case with a single-battery set. Since, as proved by practical measurements, the mean useful effect of a battery for this kind of plant is only about 65%, the efficiency of the normal plant with the single-battery system is much higher than that with a two-battery system.

Another advantage of a single-battery system is that there are never any gases or caustic vapours hanging about in the vicinity of the accumulators, because a battery maintained by a preservation charge does not gas.

Finally we come to what are possibly the most important advantages: the life of a battery maintained by a preservation charge is very much longer, as explained above, and might be said to be almost unlimited if the battery did not now and then have to come into action when the mains fail. Upkeep and attendance can be reduced to practically nil: with a single-battery system on the principle of *fig. 3* the battery functions and ceases to function without any manual aid or automatic switching, and if the rectifier is of a suitable construction (about which more will be said later) the installation can be left entirely to itself; apart from a simple manipulation after a mains breakdown, all that is required is a monthly overhaul.

### The preservation rectifier

As a characteristic feature of preservation charging it has been said above that a voltage of 2.1 to 2.2 V per cell has to be maintained on the battery. It is the satisfying of this condition that constitutes the main problem in a single-battery system.

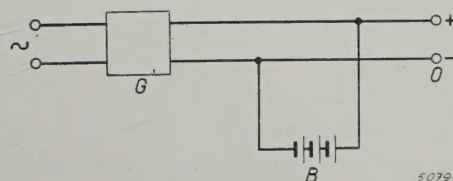


Fig. 3. A single-battery system where the plant *O* and the battery *B* are permanently connected in parallel to a preserving rectifier *G*.

With the arrangement according to *fig. 2* it is in the first place necessary that the output voltage of the rectifier should vary as little as possible with the inevitable fluctuations of the mains voltage,



which may amount to  $\pm 5\%$  and even sometimes  $\pm 10\%$ . With a system according to fig. 3, which is to be preferred because it dispenses with all switching operations and which we shall, therefore, consider exclusively from now on, something more has to be demanded of the rectifier: its output voltage must also be independent of fluctuations in the load.

Ordinary rectifiers do not by any means possess these properties. Their output voltage drops considerably the higher the power consumed, with the result that with every increase of the load the battery, connected parallel to the rectifier, takes part in supplying current to the plant and thus loses some of its charge. If the rectifier voltage drops  $10\%$  — which may well happen if both the mains voltage and the load change simultaneously — this means a dissipation of about  $80\%$  of the battery's capacity <sup>4)</sup>. Needless to say, very little then remains for the functioning of the single-battery system.

Nevertheless, for the lack of anything better the ordinary rectifier has in the past been used for this purpose. By continuous readjustment one endeavoured to make the rectifier current at any moment as far as possible equal to the current consumption plus a small excess to compensate the battery losses. Of course, this readjusting by hand is only a makeshift and only partly helps to achieve the advantages of the single-battery system. As a matter of fact in the beginning the single-battery system was mainly applied for the sake of its simplicity and the cutting out of switching operations; one was then scarcely aware of the importance of the principle of preservation charging, so that it was not fully realized what advantages were lost owing to the rectifier voltage not being kept sufficiently constant.

Once impressed with the importance of the new treatment of batteries, one had to look for a battery charger which in spite of mains voltage fluctuations and load variations continues to supply a constant d.c. voltage. Such an apparatus we will call a preservation rectifier, in view of the object of keeping a battery under a preservation charge <sup>5)</sup>. As a matter of fact a similar apparatus had already been developed for another purpose, for cases

where a constant voltage was required not for the charging of a battery but for the power plant itself. Such is particularly the case with telephone exchanges. In a previous article <sup>6)</sup> it has been explained that the supply voltage of a telephone exchange is confined to very narrow limits for a proper functioning of the automatic selectors, while on the other hand the load varies considerably owing to the varying number of telephone conversations being carried at a time. (A battery connected also as a reserve likewise benefits when for these reasons the voltage is kept constant.)

Various kinds of supply rectifiers have been worked out for this purpose. In the first place there is a group of constructions where the voltage is regulated by a resistance in the direct current circuit which automatically increases as the voltage rises. This regulation of the resistance is effected for instance by the sliding of a contact by a servomotor governed by a contact voltmeter or by a magnet coil connected to the voltage to be regulated, or by some other means, in any case mechanically. Mostly this necessitates the special measures to prevent oscillations due to the inertia of the masses to be moved. Furthermore, wear and tear is inevitable. If such an apparatus were to be used as a preserving rectifier in a supply system according to fig. 3, then a difficulty would arise in the event of mains failures of long duration, for the battery would then have given off much of its charge and its voltage will have dropped considerably. Since the regulating mechanism adjusts the output voltage of the apparatus to the normal value after the mains voltage has returned, far too high currents may result. This means that special measures have again to be taken, which make the apparatus complicated, or else it must be continuously watched and operators must be ready to take action immediately after every breakdown of the mains <sup>7)</sup>.

<sup>5)</sup> It is pointed out that this term is used here in a narrower meaning than that in which it is used in literature; generally it is taken to mean a rectifier capable of keeping an unloaded battery under a preserving charge, thus compensating the leak losses and maintaining the battery voltage at 2.1 to 2.2 volt per cell. We are using the term preserving rectifier here for an apparatus that keeps the battery voltage independent of both the mains voltage and the load within the limits mentioned.

<sup>6)</sup> H. A. W. Klinkhamer, A rectifier for small telephone exchanges, Philips Techn. Rev. 6, pp. 39-45, 1941.

<sup>7)</sup> The fact that notwithstanding these complications this kind of apparatus has frequently been used as a preserving rectifier for the single-battery system right up to the present time clearly shows what value is attached to this system. B. Stange, for instance, in E.T.Z. 64, 341-344 and 372-377, 1943, maintains that the complications with such an apparatus are more than compensated by the advantages of the single-battery system.

<sup>4)</sup> The relation between the voltage and the state of charge of a battery is not unequivocal. Only after very small quantities of the charge have been dissipated can it be said that the battery after recharging to its original voltages has again reached practically its original state of charge. If, however, the battery is discharged to a higher degree then it must be recharged for some time to an over-voltage before it gets back its full state of charge.



It has been endeavoured to overcome the drawback of mass inertia and of wear by governing the reactance of the a.c. side of the rectifier by electrical or magnetic means *via* the output voltage, instead of by mechanical means. We would mention here as an example the connecting in series of a choke pre-magnetised with the direct current.

#### A preserving rectifier with highly saturated transformer

Some years ago Philips constructed a rectifier (see the article quoted in footnote <sup>6</sup>) of such a design that the voltage is kept constant not by a regulating reactance of the output voltage but by means of a highly saturated transformer in a special circuit as represented in fig. 4b. (Fig. 4a shows the circuit of a normal rectifier by way of comparison.)

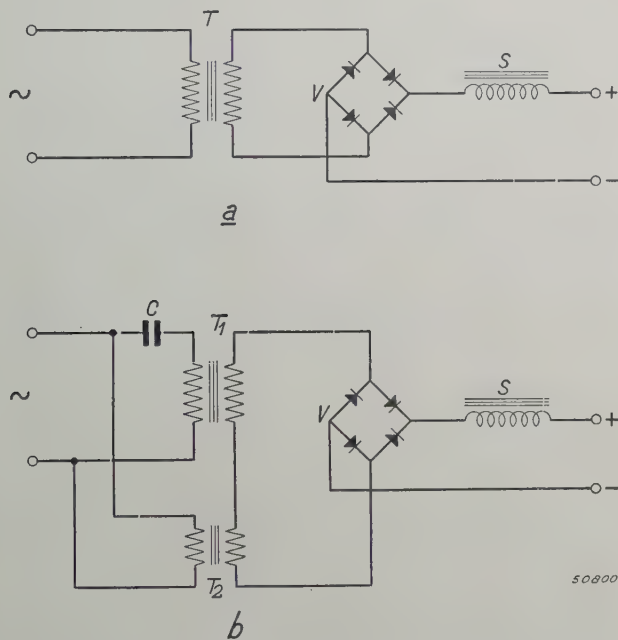


Fig. 4. Arrangement of a normal rectifier with transformer T, four selenium valves V with Graetz circuit, and smoothing choke S.

b) Arrangement with a preserving rectifier according to a principle described earlier <sup>6</sup>). T<sub>1</sub> is a transformer with highly saturated iron core, C a condenser, T<sub>2</sub> a small normal transformer, V selenium valves, S choke.

The working of this circuit is not immediately apparent. For an explanation and for the deduction of the characteristic of such a rectifier from the data of the elements and the magnetisation curve of the iron core see the article referred to in footnote <sup>6</sup>). Here we will deal only with those properties of this kind of rectifier that make them specially suitable for use as a preserving rectifier.

The direct voltage is to a very high degree independent of load and mains voltage fluctuations,

as may be seen from figs. 5 and 6. Fig. 5 gives the characteristic, *i.e.* the direct voltage as a function of the load current, for the nominal mains voltage. It will be seen that within a wide range of current

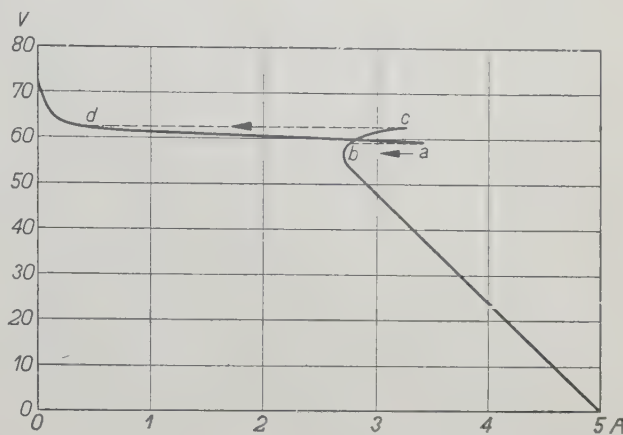


Fig. 5. Characteristic of a rectifier according to fig. 4b. The voltage varies but little within a wide range of load currents (approx. 0.3—3 Amp.). The characteristic has two branches. When the load rises to point a the working point jumps over to the steep branch (a → b), so that the current taken off continues to be limited. When the load drops the working point does not jump back to the flat branch until the voltage of the permanently connected battery has risen to point c (c → d).

intensities — in this case between approximately 0.3 and 3 amperes — the voltage varies by only a few percent (from 63-60 volt). Fig. 6 gives the characteristic for three different values of the mains voltage and shows that even with a varying mains voltage the direct voltage remains fairly constant, within about 3% for 10% mains voltage difference<sup>8</sup>).

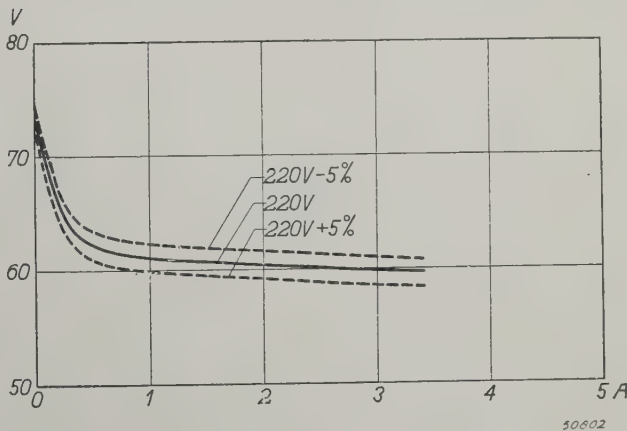


Fig. 6. Characteristics as in fig. 5 for three different mains voltages (nominal 220 V). Only the flat branch is drawn. It will be noted that the voltage rises with falling mains voltage and *vice versa*. The variations are small: about 3% for 10% mains voltage variation.

<sup>8</sup>) It should be noted that these characteristics are obtained at the nominal frequency of the mains. If the mains frequency shows considerable fluctuations, as is the case in many countries in the present post-war period, then the properties of the rectifier system described here are less favourable, in that the output voltage is not sufficiently constant.



If only on this account the apparatus is therefore already capable of answering the requirements of a preserving rectifier, whilst, moreover, it has the advantage of the absence of inertia and wear, since there are no moving parts. But from a closer investigation it will be found to have yet another important property which avoids in a simple manner the last of the drawbacks mentioned above as attaching to former constructions, *i.e.* the necessity of manual manipulations immediately after a mains breakdown. As may be seen from fig. 5, the characteristic of the rectifier consists of two separate intersecting branches, one flat and one steep. The rectifier is so designed that for the current intensities normally required for the plant the working point always lies on the flat branch. Variations in the state of charge of the battery are thereby extremely limited. Should a load peak arise which is too great for the highest current of the flat branch then the rectifier adjusts itself, the working point jumping over to the steep branch from *a* to *b* along the lower dotted line (see fig. 5). The battery then supplies that part of the total current that is lacking. When the peak has passed the working point it remains for a moment on the steep branch of the characteristic, the rectifier thus supplying more current than is being consumed by the plant, and this surplus serves to charge up the battery again. As the battery voltage rises so the working point climbs along the steep branch until the point *c* is reached, where the rectifier readjusts itself, the working point jumping back along the upper dotted line to the flat branch, towards point *d*.

In the event of the mains failing then the battery comes into full operation and is discharged more or less according to the duration of the mains breakdown. Even though the mains interruption may last so long as to cause the battery voltage to drop considerably, when the mains voltage comes on again there need be no fear of very high currents arising. As a matter of fact the working point of the rectifier then immediately comes to lie on the steep branch of the characteristic, at the level corresponding to the battery voltage at that moment. Consequently the current continues to be limited and can never reach a dangerous level, while this does not call for any manual action. During the normal working the battery is then charged up again until the battery voltage reaches the top of the steep branch (point *c*).

The battery is not then fully charged, it is true, because charging would have to continue for a time at a still higher voltage. For that purpose a small "booster" is built into the rectifier, which

can be connected, automatically or otherwise, in series with the rectifier proper to get quick charging, dropping out of action as soon as the desired voltage of the battery is reached. Even though the booster may not have automatic action it involves no extra work worth mentioning: since it is only a matter of a supplementary charging it is not necessary to boost up immediately after a mains failure, for this can be done within a day or two by sending someone to switch on the booster. If another small preserving rectifier is used as booster then no supervision at all is required for rapid charging.

In fig. 5 it is seen that the characteristic rises steeply on the extreme left. Consequently the voltage on the battery would there be higher than is normally desired. In most cases of normal working, however, this point is never reached, for the working point can only reach such a position if the installation remains entirely unloaded for one or two days. But even if the working point should reach this area there would still be no harm done to the battery, because the current intensity with which the battery is then further charged is extremely low. If necessary that rising part of the characteristic can, as a matter of fact, be removed by applying a small rest-load.

All these properties of this preserving rectifier make it possible to leave the accumulator battery to look after itself, apart from an inspection say once a month. We thus have the full benefit of all the advantages of the single-battery system: lasting qualities of the battery, practically its full capacity being available in case of need, simplicity of the circuit, continued working of the plant in case of mains failure without switching operations and without any interruption, functioning without attendance and practically no supervision.

### Some special applications of preserving rectifiers

It should by now be sufficiently clear why we regard the single-battery system with a preserving rectifier of the construction described here as the ideal emergency supply system for all sorts of cases. We will now mention a few special cases where the preserving rectifier is used in somewhat different ways.

One application for telephony has already been fully dealt with in the article quoted in footnote<sup>6</sup>). In that case the preserving rectifier with battery served for the feeding of terminal exchanges in the telephone network. In these small exchanges, where there are no permanent attendants, the properties of these rectifiers show to their fullest advantage.

But also in larger telephone exchanges where personnel are always in attendance the advantages



of this system are still of importance. Such has proved to be the case with a trial installation taken into use some years ago in a so-called junction exchange of the Dutch P.T.T. In these exchanges the daily variation of load differs from that in the terminal exchanges; there is also a certain permanent (rest) load due to the counting apparatus for the trunk calls. This does not, however, make any essential difference for the action of the rectifier and the battery.

For this trial installation the capacity required was about five times that needed for terminal exchanges. The designing of a preserving rectifier for high ratings is a somewhat more difficult problem than that of increasing the capacity in the case of normal rectifiers. Owing to the high saturation of the transformer core the iron losses in a preserving rectifier of the type described are greater than

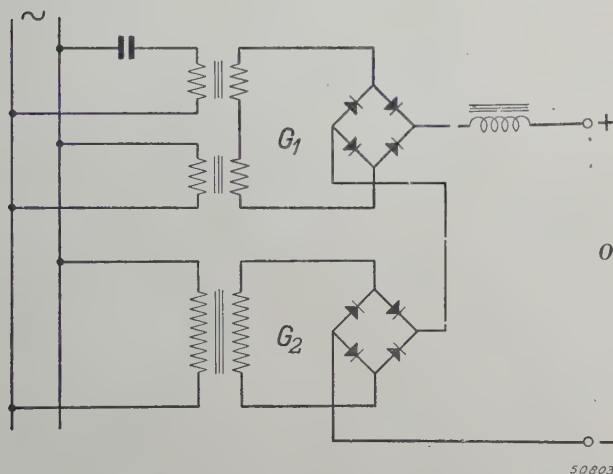


Fig. 7. Series connection of a preserving rectifier  $G_1$  and an ordinary rectifier  $G_2$ . A similar arrangement is being used for the feeding of a number of junction exchanges of the Dutch P.T.T.

normal, that is to say the heating that arises becomes troublesome already with small transformer volumes. For this reason it is more economical in the case of higher capacities not to rely solely upon a preserving rectifier for the supply of the total power but to have such a rectifier connected in series with an ordinary battery charger. This also has the advantage that the influence of mains voltage fluctuations can be still further restricted, for, as shown in fig. 6, the output voltage of the type of preserving rectifier described rises as the main voltage of a normal rectifier drops with falling mains voltage, and when we have the two connected in series these effects partly neutralize each other. This was utilised in the installation for a junction exchange. The power required (15 Amp., 60 V) is supplied for 3/4 by a preserving rectifier and for

1/4 by an ordinary battery charger. Fig. 7 is a diagram of the set-up that has now already been applied for several junction exchanges. With a mains voltage variation of 10% the direct voltage

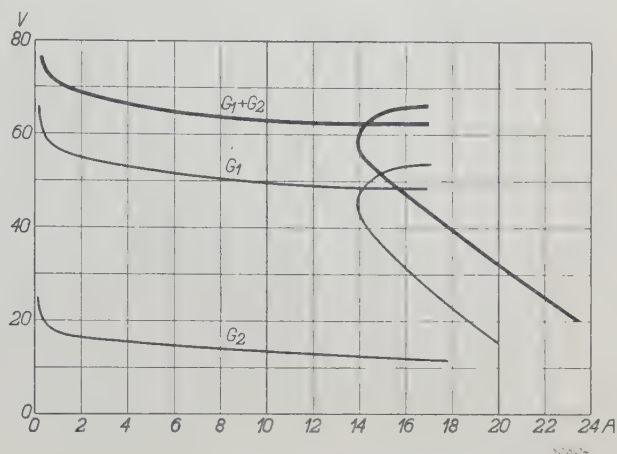


Fig. 8. Characteristics of the two rectifiers of fig. 7, each taken separately:  $G_1$ ,  $G_2$ ; the resulting characteristic of the series connection of the two rectifiers is  $G_1 + G_2$ .

varies by only 1%. Fig. 8 gives the characteristics of the two rectifiers when each is used separately, as also the resulting characteristic when the two are connected in series. It is remarkable that in spite of the steep slope of the characteristic  $G_2$  the resultant characteristic is not noticeably steeper than  $G_1$ . Consequently the effect of load variation on the output voltage is not greater with the series connection than with the preserving rectifier alone. This is quite understandable when it is borne in mind that the moments of opening and closing

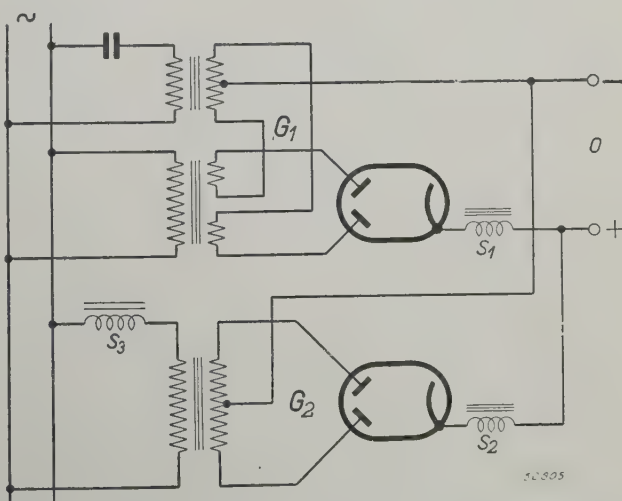


Fig. 9. Parallel circuiting of a preserving rectifier  $G_1$  and an ordinary rectifier  $G_2$ . In the special case where we applied this arrangement it was desirable to use rectifying valves instead of selenium valves.  $S_1$  and  $S_2$  are chokes.  $S_3$  is a variable choke by means of which the flat part of the resulting characteristic (see  $G_1 + G_2$  in fig. 10) can be shifted to the desired current intensity range.



of the valves for the two rectifiers connected in series are not mutually independent. One may not therefore simply add together the ordinates of the two characteristics for each abscissa (current intensity). (The theoretical deduction of the actual course of the resultant characteristic is very difficult.)

characteristic of the two rectifiers and the resultant characteristic of the parallel connection. Since the output voltages in this case are identical, the two rectifiers here do indeed behave independently of each other and the resultant characteristic is obtained simply by adding the two abscissae for each ordinate. It is seen that the resultant charac-

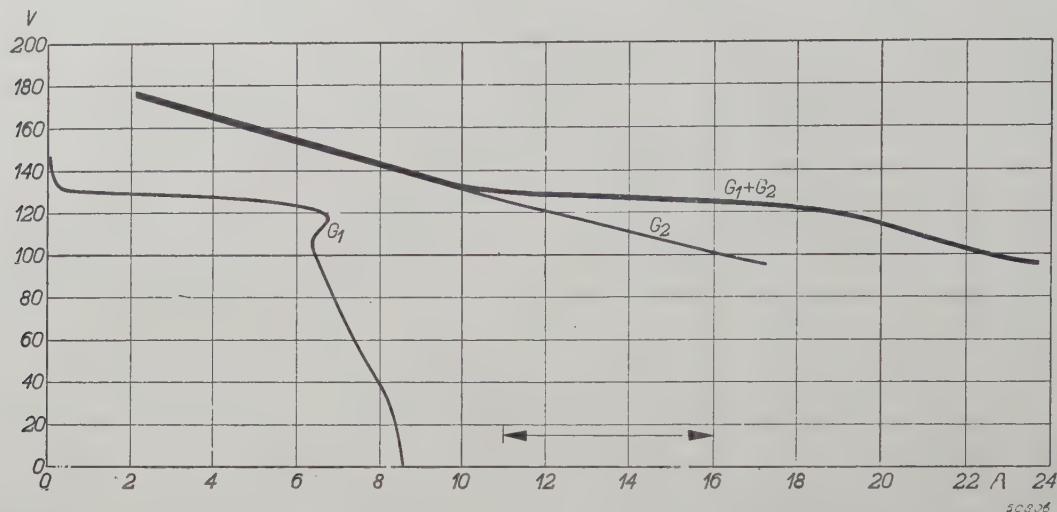


Fig. 10. Characteristics  $G_1$  and  $G_2$  of the two rectifiers of fig. 9 each taken separately. Since the internal resistance of a rectifying valve varies with the current in a manner different from that of a selenium valve, the characteristic  $G_1$  differs somewhat from that in fig. 5; though there is a flat and a steep branch these flow into each other without intersecting.  $G_1 + G_2$  is the resulting characteristic of the parallel circuiting of the two rectifiers. Within a limited current intensity range (indicated on the abscissa) the voltage is fairly constant, whilst only a relatively small part of the power has to be supplied by the preserving rectifier.

A somewhat different manner of coordinated action between an ordinary rectifier and a preserving rectifier is obtained when these are connected in parallel. Such an arrangement has been applied, for instance, for the feeding of a set of magnetic mains switches in a distributing station of the electrical network of the Philips works. The set-up is shown in fig. 9, whilst fig. 10 gives the separate

characteristic has a fairly steep slope on the whole but that in a small range it is practically horizontal. In the case in question it was in fact only a matter of a small range of current intensities, so that the arrangement described had the advantages that the horizontal part of the characteristic could be attained in that small range with a quite small and thus inexpensive preserving rectifier.



# SEMI-CONDUCTORS WITH LARGE NEGATIVE TEMPERATURE COEFFICIENT OF RESISTANCE

by E. J. W. VERWEY, P. W. HAAYMAN and F. C. ROMEYN.

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In view of the increasing importance in electrotechnology of resistor materials having a large negative temperature coefficient of resistance, materials having this property have been developed in the Philips laboratories. These materials are mixed crystals of  $\text{Fe}_3\text{O}_4$  with certain substances having the same crystal structure as  $\text{Fe}_3\text{O}_4$ , the so-called spinel structure. They offer considerable advantages compared with the materials hitherto used for this purpose. In the first place they are much more constant in manufacture: their resistivity is exclusively governed by the mixing proportions of  $\text{Fe}_3\text{O}_4$  and the other component. In the second place the electrical properties (the values of the resistance and its temperature coefficient) of the resistors made with these materials — here called *h.t.c. resistors* — are much more constant in use: for most applications a h.t.c. resistor can be used in air without requiring any special precautions, even at a temperature of some hundred degrees centigrade.

This article deals with the practical possibilities of these resistors and the physical-chemical background underlying the development of these new materials.

## Introduction

Semi-conductors are solids whose specific resistivity is much greater than that of metals. The conduction mechanism in semi-conductors may be based either on the movement of ions (electrolytic conduction) or on that of electrons (electronic conduction). Only the electronic semi-conductors are employed in practice as materials for resistors, because electrolytic conduction is accompanied by chemical changes and polarization phenomena which are found to be troublesome. In this article, therefore, we are dealing only with the electronic semi-conductors.

Although the conduction in these semi-conductors is due to the same movement of electrons as occurs in metals, the mechanism of that phenomenon is essentially different from that in the metals. This manifests itself in the fact, among others, that with increasing temperature the specific resistivity of these semi-conductors diminishes, whereas in the case of the metals it is the other way round. It appears that the relation between the specific resistivity  $\rho$  of semi-conductors and the absolute temperature  $T$  can be expressed in good approximation by the formula

$$\rho = \rho_{\infty} e^{b/T} \dots \dots \dots (1)$$

where  $\rho_{\infty}$  and  $b$  are positive temperature-independent constants. The temperature coefficient  $\alpha$  of the resistance is therefore

$$\alpha = \frac{1}{\rho} \frac{d\rho}{dT} = -\frac{b}{T^2}, \dots \dots \dots (2)$$

and thus decidedly negative.

For electric circuits a resistance with a negative

temperature coefficient (abbreviated: t.c.) obviously offers certain advantages. It is for this reason too that semi-conductors are so highly important in electrotechnology. But in their application semi-conductors have often turned out to be less satisfactory than was to be expected. This is due to the fact that for practically all semi-conductors hitherto employed the electrical properties — the value of the resistance and of the t.c. — are subject to considerable changes in use; moreover, in the manufacture of semi-conductors it has generally been very difficult to get absolutely invariable results.

In the course of the last few years, however, the Philips laboratories have been developing semi-conductors which have a highly negative t.c. and exhibit these two disadvantages to a very much less extent. These semi-conductors are mixed crystals and compounded of  $\text{Fe}_3\text{O}_4$  with certain substances satisfying the general chemical formula  $\text{XY}_2\text{O}_4$ . An essential requirement is that these substances must have the same crystal structure as  $\text{Fe}_3\text{O}_4$  (this chemical formula may also be written as  $\text{FeFe}_2\text{O}_4$ ), the so-called spinel structure. The resistors made from these semi-conductors are here called *h.t.c. resistors*. The properties of these h.t.c. resistors are fairly stable, so that they can be used in air, even at a temperature of some hundred degrees centigrade, without any special precautions. They are also very well reproducible: in the manufacture of the material for h.t.c. resistors the desired value of resistivity can easily be obtained by a suitable choice of the mixing proportions of  $\text{Fe}_3\text{O}_4$  and the other component.

It is to be pointed out that the use of h.t.c.



resistors is not confined to those cases where materials with a negative t.c. are needed. It has been found that the absolute value of the t.c. of h.t.c. resistors at room temperature is larger than that of metals by a factor 10. Consequently if the action of any particular instrument is based upon the variability of the resistance with temperature and it makes no essential difference whether the t.c. is positive or negative, it will often be easy to increase the sensitivity of the instrument by using a h.t.c. resistor instead of a metallic one.

The possibilities of the h.t.c. resistors will be discussed more fully in the first section of this paper. There will then follow an explanation of the physical-chemical background underlying their development. This will be done with reference to two articles recently published in this journal, one on the electronic conduction in semi-conductors<sup>1)</sup> and the other on materials having the spinel structure<sup>2)</sup>. It will be found that the good stability of h.t.c. resistors and constancy of their electrical properties are easily understandable from the conduction mechanism of the semi-conductors (which becomes evident, *inter alia*, from equation (1)) and from the characteristics of the spinel structure.

#### Applications of h.t.c. resistors

The uses to which h.t.c. resistors can be put may be placed under two headings, one where the t.c. must be essentially negative and the other where only the high absolute value of the t.c. is of importance.

#### *Applications where the t.c. must be essentially negative*

Here two cases may be distinguished. In the first case good use is made of the fact that it takes some time for the current to heat up the h.t.c. resistor and for equilibrium to be reached between the electrical energy supplied (Joule heat) and the heat carried off through convection, conduction and radiation. In the second case the h.t.c. resistor is used in a state of equilibrium; the inertia of the phenomenon is then taken into account or else attempts are made to reduce it by special measures.

A typical example of the first case is to be found in radio technique. In radio valves with an indirectly heated cathode it takes some time before the cathode reaches its ultimate temperature. The t.c. of the heater filaments (generally of tungsten) being positive, their resistance is lower when the current is first switched on than it is in the ultimate state.

Where the heater filaments are connected in series with other parts of the circuit it may therefore happen that when the current is switched on those other parts have to withstand a much greater voltage than prevails during the normal working. The consequences for the parts in question may be fatal. This difficulty can now easily be circumvented by connecting a h.t.c. resistor in series with the heater filaments. The resistivity and the dimensions of the h.t.c. resistor can easily be chosen of such a value that at the initial temperature the dangerous over-voltage is practically entirely taken up by the h.t.c. resistor, while thanks to its highly negative t.c. this resistance cuts itself out almost completely at the higher final temperature of the resistance. The principle of this application of h.t.c. resistors is of course not limited to radio sets but can also be applied, for instance, for lowering switch-on peaks such as occur with motors.

As regards the second kind of application we have to consider further the current-voltage characteristic of the h.t.c. resistors in the stationary state. This is represented diagrammatically in *fig. 1*, where

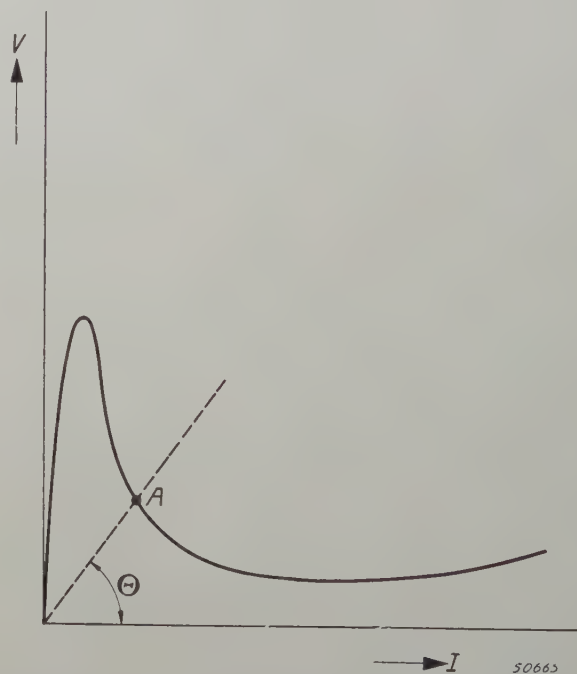


Fig. 1. The voltage  $V$  across a h.t.c. resistor as function of the current intensity  $I$  (qualitative). At a certain value of  $I$  the resistivity is given by  $\tan \Theta$ .

the voltage  $V$  across the resistance is plotted as a function of the current  $I$  flowing through the resistor. For a certain current the value  $R$  of the resistance is given by the tangent of the angle  $\Theta$  between the horizontal axis and the line drawn from the origin through the "working point"  $A$ . The higher the intensity of the current, the higher is the tempera-

<sup>1)</sup> Philips Techn. Rev. 9, 46-54, 1947 (No. 2).

<sup>2)</sup> Philips Techn. Rev. 9, 186-192, 1947 (No. 6).



ture of the resistor and, owing to the negative sign of the t.c., the smaller the value of the resistance. The reduction of the resistance with increasing current intensity becomes more gradual as the current intensity becomes greater.

The remarkable shape of the characteristic can be understood when it is considered that in the state of equilibrium the Joule heat generated in the resistor must be equal to the heat carried off to the outside. The precise form of the characteristics will therefore depend not only upon the electrical properties of the h.t.c. resistor, but also upon the manner in which heat is exchanged with the surroundings. Consequently in a vacuum a h.t.c. resistor will behave differently than in a gas.

Now several parts of this characteristic can be used in electric circuits. First of all it is seen that over a large part of the curve the voltage varies but little with the current intensity, namely in that part corresponding to high loads. This kind of resistor can therefore be used as a voltage stabilizer.

Secondly, there is a part of the curve having a negative slope, thus corresponding to a negative differential resistance  $dV/dI$ . Since negative differential resistances play a part in the excitation of electric vibrations, we have here another field open for the use of h.t.c. resistors, at least for low frequencies.

The combination of an ordinary "temperature-independent" resistor and a h.t.c. resistor in series again produces a horizontal straight line within a certain range of the  $V$ - $I$  characteristic, as may be seen from fig. 2. Such a combination of resistors can therefore also be used for the stabilization of voltage. In many cases this has advantages not obtained when using the flat part of the characteristic of the h.t.c. resistor itself: the horizontal part of the characteristic lies at a much lower current intensity; there is no maximum having to be exceeded before the condition is reached corresponding to the horizontal part of the characteristic.

In all these applications a h.t.c. resistor will reach the state of equilibrium more quickly and the fluctuations of the voltage or of the current follow accordingly when (a) the thermal capacity of the resistance is lower and (b) the heat exchange with the surroundings is more rapid. In connection with (a) these resistors can be applied in the form of very thin wires. This is made possible by employing the known ceramic methods, as for instance by spraying the ceramic mass with a suitable binder, and then baking the wires in a hanging position. As regards (b) this can be brought about by placing

the resistor in a small tube filled with a gas consisting of very light molecules (e.g. helium).

Among the group of applications being dealt with here there is also the case where a resistance has to be provided which is independent of the

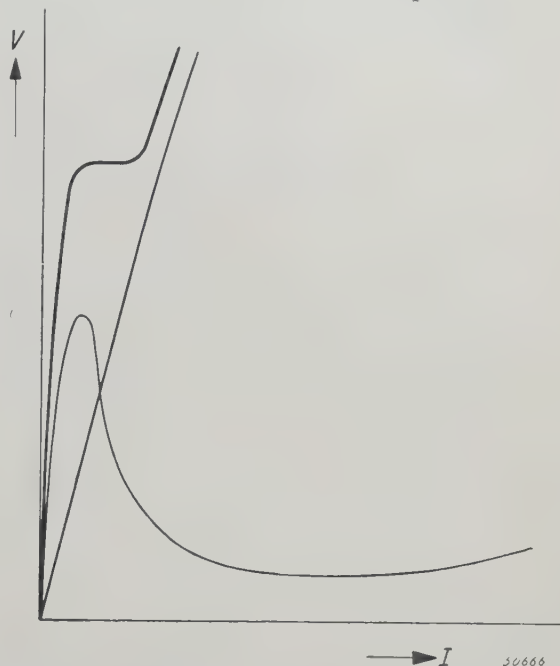


Fig. 2. The voltage  $V$  across a resistor comprising a h.t.c. resistor in series with a metallic resistor, as function of the current intensity  $I$  (qualitative).

ambient temperature within a certain temperature range. This is again attained by connecting a suitably dimensioned h.t.c. resistor in series with a metallic resistor.

*Applications where the high absolute value of the t.c. is of importance.*

As already indicated in the introduction, here we have in mind the application of h.t.c. resistors in all kinds of instruments whose action is based on a t.c. differing from zero and in which it is in principle immaterial whether the t.c. is positive or negative. In the past metallic temperature-dependent resistors have usually been used for this purpose — for instance resistance thermometers or bolometers. The sensitivity of such instruments is greater the higher the absolute value of the t.c.

Now the specific resistivity  $\varrho_{\text{met}}$  of metals at not too low a temperature is approximately proportional to the absolute temperature  $T$ :

$$\varrho_{\text{met}} = \text{const. } T.$$

From this it follows that the t.c. of  $\varrho_{\text{met}}$  is practically independent of the value of  $\varrho_{\text{met}}$ . In other words the t.c. has approximately the same value for all metals:



$$\alpha_{\text{met}} = \frac{1}{\varrho_{\text{met}}} \frac{d\varrho_{\text{met}}}{dT} = \frac{1}{T},$$

that is to say at room temperature  $T = 300^\circ$  and  $\alpha_{\text{met}} = 0.33\%$ .

In the case of semi-conductors the situation is quite different. Here  $\alpha$  is indeed dependent upon the value of the specific resistivity, for from equations (1) and (2) it follows that

$$\alpha = \frac{\log \varrho_\infty - \log \varrho}{T}.$$

From the point of view of measuring technique a specific resistivity of  $10^5 \Omega \text{ cm}$  is quite suitable. Assuming further that  $\varrho_\infty = 10^{-2} \Omega \text{ cm}$  (a still lower value of  $\varrho_\infty$  is as a matter of fact not difficult to attain) then with the aid of the last formula we find:

$$\alpha = \frac{-2.5}{T} (\log 10) \approx -\frac{16}{T}.$$

For a h.t.c. resistor for which  $\varrho = 10^5 \Omega \text{ cm}$  is at room temperature it follows that  $\alpha \approx 5\%$ .

The superiority of h. t. c. resistors compared with metallic resistors is therefore obvious, apart from the further consideration that the high value of the specific resistivity is in itself an advantage in resistance thermometry.

Long-wave infra-red rays cannot be investigated with the aid of photo-conduction, photo-electrical emission or photographic methods, since the energy quanta are too small, so that bolometers have to be employed. For these bolometers h. t. c. resistors can be made in the form of thin membranes provided on either side with a metallic contact. The area of the surface chosen will generally be such that the beam just radiates the whole membrane. The membranes have to be very thin to keep their thermal capacity very low, this being favourable for the starting time of the instrument.

H. t. c. resistors are also suitable for measuring energy at still longer wavelengths, in the range of radio waves of very high frequency (cm waves). They are then used in the form of very small balls (size of a pin's head) with two very thin metal filaments baked in to serve as contacts.

In all these applications the measuring current sent through the resistor has to be sufficiently weak as not to cause any measurable change in the temperature of the resistor. Thus the value of the resistance is practically exclusively governed by the energy supplied (in the form of heat or radiation), as opposed to the case of the first group of applications, where the equilibrium temperature of the resistor and

thus also the value of the resistance are dependent upon the Joule heat of the current.

Another possibility coming under this group of applications is the case where the temperature and in consequence the resistivity of a h. t. c. resistor is regulated by an external heating current. The current in one circuit can be continuously controlled with the aid of the current in another circuit, with the two circuits completely separated electrically. In such a case a h. t. c. resistor can be used, for instance, in the form of a slender rod surrounded by a coiled metal wire in such a way that a small space is maintained between the two conductors over the entire length, this assembly, with leads, then being mounted in an evacuated envelope or a tube filled with an inert gas.

To conclude this summary of the possibilities of h. t. c. resistors we would mention that apart from the shapes already spoken of (thin filaments, membranes, minute balls) these resistors can also be made in the form of small rods, plates, tubes, etc.

#### The physical-chemical background underlying the development of h. t. c. resistors

##### *The temperature-dependance of the resistance in semi-conductors*

In a good conductor, for instance a metal, the conduction electrons are more or less free. When the temperature rises the number of free electrons remains unchanged. The electrical resistance, however, increases, owing to the fact that at a higher temperature the electrons become more scattered and are checked in their motion by the increased thermal movement of the atoms.

In semi-conductors the situation is quite different. At low temperature the material contains no free electrons. In the article quoted in footnote <sup>1)</sup> we saw, however, that by introducing either optical energy or thermal energy the electrons can be given more or less freedom of movement in the crystal lattice. If only little energy is required for this, that is to say if the electrons are only "weakly bound", it may happen that the material will already have considerable conductivity at room temperature. Anyhow, the number of electrons released by the thermal energy increases rapidly with the temperature. This effect as a rule exceeds by far the other effect of increased scattering and checking of the electrons. As a result the electric resistance diminishes rapidly with rising temperature; in other words the temperature coefficient of resistance is negative.

The relation (1) between the value of the resistance and the temperature is obtained roughly



as follows. Let us suppose that in the crystal lattice there are  $N$  places occupied by weakly bound electrons and that an energy  $\varepsilon$ , called the activation energy, is required to give such an electron more or less freedom of movement. At the absolute temperature  $T$  there will be on an average  $n$  of the  $N$  electrons in a more or less free state, that is to say there will be interstices in  $n$  of the said  $N$  places. In the thermo-dynamic equilibrium the relation then holds:

$$\frac{n \cdot n}{N-n} = \text{const.} \cdot e^{-\varepsilon/kT},$$

in which  $k$  is Boltzmann's constant <sup>3)</sup>. Since  $n$  is much smaller than  $N$  we may also write this formula as follows:

$$n = \text{const.} \cdot \sqrt{N} e^{-\varepsilon/2kT}.$$

The specific conductivity is now equal to the product of the mobility of the electron in the more or less free state and  $n$ , if the latter number is taken per cubic centimeter. Since the mobility of electrons is practically independent of temperature, ultimately we actually get for the temperature-dependence of the specific resistivity a formula of the form (1), where  $b = \varepsilon/2k$ :

$$\varrho = \text{const.} \cdot e^{b/T} \dots \dots \dots (3)$$

#### Temperature-dependence of the resistance of $\text{Fe}_3\text{O}_4$

After this introduction we will now proceed to discuss the semi-conductors from which h.t.c. resistors are made. The basic material, as stated in the introduction, is the compound  $\text{Fe}_3\text{O}_4$ , known in its mineral form under the name of magnetite and sometimes also called ferro-ferrite because it can be regarded as a ferritic  $\text{MFe}_2\text{O}_4$ , with bivalent iron playing the part of the metal  $M$ . This substance is a fairly good electron conductor, even a very good conductor compared with other oxidic semi-conductors: the specific resistivity at room temperature amounts to  $5 \times 10^{-3} \Omega \text{ cm}$ , thus only a few hundred times the specific resistivity of metals. Yet  $\text{Fe}_3\text{O}_4$  is a semi-conductor, in the sense that within a large temperature range it satisfies approximately the law (1). This is demonstrated in fig. 3, giving the logarithm of the specific resistivity  $\varrho$  of  $\text{Fe}_3\text{O}_4$  as a function of  $1/T$  (in this graph the temperature increases from right to left). We will first consider that part of the curve lying between approximately  $130^\circ\text{K}$  and  $200^\circ\text{K}$ . Here the resistivity increases with

falling temperature, the curve approaching a straight line. This is in agreement with equation (1), for from this equation it follows that:

$$\log \varrho = -\frac{b}{T} + \log \varrho_\infty, \dots \dots (4)$$

so that  $\log \varrho$  is indeed a linear function of  $1/T$ . Further, we see that this practically linear part of the curve has only a small slope. In the temperature range for which  $T > 200^\circ\text{K}$  the curve runs almost horizontal; for  $T > 300^\circ\text{K}$  (this part of the

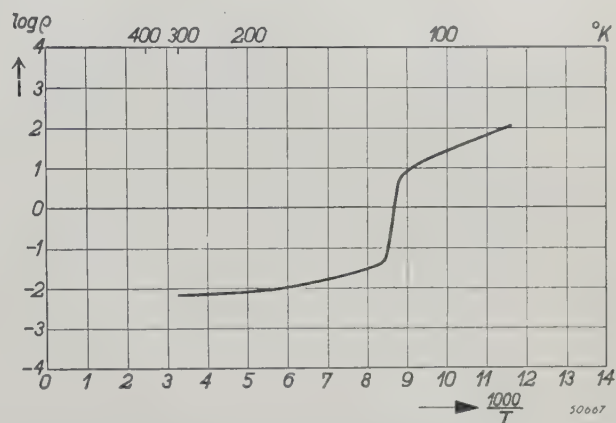


Fig. 3. Logarithm of the specific resistivity  $\sigma$  (in  $\Omega \text{ cm}$ ) as function of  $1/T$ , where  $T$  is the absolute temperature, for  $\text{Fe}_3\text{O}_4$ .

curve is not drawn in the graph) the t.c. becomes even positive. Presumably here the metallic effect of increased scattering and checking of the electrons becomes predominant; moreover,  $b$  is presumably no longer small compared with  $N$  (cf. the deduction of equation (3)).

In the right-hand part of the graph, i.e. at very low temperature, we see a peculiar phenomenon which is only observed with this substance <sup>4)</sup>  $\text{Fe}_3\text{O}_4$ , in contrast to its behaviour previously discussed. At about  $130^\circ\text{K}$  the resistivity jumps suddenly and as the temperature is further reduced the slope of the curve, i.e. the t.c., increases discontinuously. It would lead us too far afield here to enter upon a closer discussion of the nature of this transition point (see the article quoted in footnote <sup>4)</sup>). Suffice it to add that this point disappears as soon as the  $\text{Fe}_3\text{O}_4$  contains a small quantity (less than 1%) of another spinel — an abbreviation for a substance having the spinel structure.

From the foregoing it is evident that the compound  $\text{Fe}_3\text{O}_4$  alone is not usually <sup>5)</sup> suitable for the

<sup>3)</sup> A more exact resolution of this formula shows that the factor by which the exponential function is multiplied is slightly dependent upon temperature.

<sup>4)</sup> See E. J. W. Verwey and P. W. Haayman, *Physica, The Hague*, **8**, 979, 1941.

<sup>5)</sup> In a very special case use can be made of the great change in resistance at the point of transition.



applications described in this article. Both its specific resistivity and its t.c. are much too small <sup>6)</sup>. Nevertheless,  $\text{Fe}_3\text{O}_4$  is quite a suitable basis for the preparation of suitable resistance materials. Now in order to make the development of h.t.c. resistors understandable we must discuss somewhat more closely the reason for the larger specific conductivity of  $\text{Fe}_3\text{O}_4$  which is extraordinarily high for semi-conductors.

*Relation between the electron conductivity and the spinel structure of  $\text{Fe}_3\text{O}_4$*

The explanation of the high specific conductivity of  $\text{Fe}_3\text{O}_4$  is closely related to a typical property of the spinel structure of this substance. This spinel structure has already been fully dealt with in a previous article in this journal (see note 2). There it was shown that the metal atoms or ions <sup>7)</sup> in the spinel structure may be arranged in at least two ways, there being two kinds of holes available for the metal ions in this crystal structure, namely per molecule one so-called tetrahedral hole and two octahedral holes. In the case, for instance, of a spinel with the chemical formula  $\text{M}^{2+}\text{M}_2^{3+}\text{O}_4$  where  $\text{M}^{2+}$  and  $\text{M}^{3+}$  are respectively bivalent and trivalent metals, the two ways in which the metal ions may occupy the available holes are as follows. In the one type of structure the tetrahedral holes are occupied exclusively by  $\text{M}^{2+}$  and the octahedral holes exclusively by  $\text{M}^{3+}$ . In the second type of structure all the  $\text{M}^{2+}$  ions are in the octahedral holes, whilst half of the  $\text{M}^{3+}$  ions are in octahedral and the other half in tetrahedral holes; the distribution of the  $\text{M}^{2+}$  and  $\text{M}^{3+}$  ions among the octahedral holes is quite irregular. The first type of structure is indicated by the formula  $\text{M}^{2+}(\text{M}_2^{3+})\text{O}_4$  and the second by  $\text{M}^{3+}(\text{M}^{2+}\text{M}^{3+})\text{O}_4$ , the symbols of the ions situated in the octahedral holes being bracketed in each case. There are also spinels with the chemical formula  $\text{M}_2^{2+}\text{M}^{4+}\text{O}_4$  which likewise have two possible types of structure similar to these.

In the article referred to it has been seen further that it is not possible to determine directly by X-ray analysis to which type of structure  $\text{Fe}_3\text{O}_4$  belongs. A number of "rules" have, however, been used making it possible to predict with a great

degree of probability the arrangement of the metal ions in a certain substance with spinel structure. In a somewhat abbreviated form the rules in question are:

- 1) The trivalent and quadrivalent metal ions occupy the octahedral holes.
- 2) Exceptions are the  $\text{Fe}^{3+}$ -ions, which preferably occupy the tetrahedral holes.
- 3)  $\text{Zn}^{2+}$ - and  $\text{Cd}^{2+}$ -ions are capable of driving the  $\text{Fe}^{3+}$ -ions out of the tetrahedral holes.

According to these rules, therefore,  $\text{Fe}_3\text{O}_4$  should have a structure of the second type,  $\text{Fe}^{3+}(\text{Fe}^{2+}\text{Fe}^{3+})\text{O}_4$ . In other words, in the octahedral holes  $\text{Fe}_3\text{O}_4$  will have a "mixture" of bivalent and trivalent ferri ions. It is to this fact that we turn for an explanation of the exceptionally high conductivity of this compound, because if  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  are indeed irregularly distributed among crystallographically equal sites the transition of an electron from an  $\text{Fe}^{2+}$ -ion to an  $\text{Fe}^{3+}$ -ion (the former becoming an  $\text{Fe}^{3+}$ -ion and the latter an  $\text{Fe}^{2+}$ -ion) will make little difference in this arbitrary distribution. Since, moreover, the electric field from the surrounding ions at two crystallographically equal sites is equal, the energy of the electron before and after the transition will likewise be practically equal. Furthermore this transition may take place simultaneously in a large number of places. This is a rather extraordinary situation and the exceptionally low value of the activation energy for  $\text{Fe}_3\text{O}_4$  will no doubt be connected with it. Thanks to this low activation energy the additional electrons contained in the  $\text{Fe}^{2+}$ -ions (compared with the  $\text{Fe}^{3+}$ -ions) are more or less free (since in the octahedral holes in  $\text{Fe}_3\text{O}_4$  there are precisely just as many  $\text{Fe}^{2+}$ -ions as  $\text{Fe}^{3+}$ -ions, there are half as many electrons as there are octahedral holes available.) Just as is the case with the conduction electrons in a metal, these electrons can hardly be localised and are to be regarded rather as belonging to the whole of the ferri ions in the octahedral holes. They are continuously moving about in the lattice and thus give rise to the high conductivity of  $\text{Fe}_3\text{O}_4$ .

If the basic point (arbitrary distribution of the  $\text{Fe}^{2+}$ - and  $\text{Fe}^{3+}$ -ions among the octahedral holes) of this argument and the argument itself are correct, then when the  $\text{Fe}^{3+}$ -ions in the octahedral holes are replaced by other trivalent ions the conductivity should drop considerably. The fact that this is so has been confirmed by making mixed crystals of  $\text{Fe}_3\text{O}_4$  with other spinels. An exceptionally simple case is that of the mixed crystal  $\text{Fe}_3\text{O}_4$  and  $\text{FeAl}_2\text{O}_4$ . When these two compounds are mixed in the molecular proportion of 1:1 precisely one of every two

<sup>6)</sup> Large (negative) values of the t.c. are often met with in semi-conductors with a high specific resistivity. The fact that these two properties are often coupled together can be understood from equations (2) and (4); in so far as the term  $\log \varrho_\infty$  in equation (4) may be ignored both the logarithm of the specific resistivity and the t.c. are proportional to the same quantity  $b$ .

<sup>7)</sup> Here one may indeed speak of metal ions, since the oxidic compounds referred to here in any case somewhat approximate the ionic bond type and may be included among the so-called polar compounds.



$\text{Fe}^{3+}$ -ions is replaced by an  $\text{Al}^{3+}$ -ion. With this mixed crystal we have, on the one hand, been able to establish by X-ray analysis that  $\text{Al}^{3+}$ -ions have been substituted for the  $\text{Fe}^{3+}$ -ions in the octahedral holes, from which it was deduced with the aid of our rules that the structure of this mixed crystal is of the type  $\text{Fe}^{3+}(\text{Fe}^{2+}\text{Al}^{3+})\text{O}_4$ . On the other hand we found that the specific conductivity of this mixed crystal is only  $0.004\ \Omega^{-1}\text{ cm}^{-1}$ , whereas that of  $\text{Fe}_3\text{O}_4$  is  $200\ \Omega^{-1}\text{ cm}^{-1}$ .

Temperature-dependence of the resistance of mixed crystals of  $\text{Fe}_3\text{O}_4$  and a non-conducting spinel

In the light of what has been said above it will not be so very surprising that useful resistance materials can be obtained by making mixed crystals from  $\text{Fe}_3\text{O}_4$  and another, non-conducting, spinel. Since as a rule any two spinels easily form mixed crystals we have in principle a very wide choice. For instance one can take another ferrite, or one may use spinels built up from entirely different ions, such as  $\text{MgAl}_2\text{O}_4$ ,  $\text{MgCr}_2\text{O}_4$ ,  $\text{ZnCr}_2\text{O}_4$ ,  $\text{Zn}_2\text{TiO}_4$ , etc., or maybe a combination of these spinels. Speaking generally, one may say that — as is to be expected from the foregoing — the higher the content of foreign spinel the higher the specific resistivity and likewise the t.c.

An example is the system  $\text{Fe}_3\text{O}_4\text{-ZnCr}_2\text{O}_4$ , for which the relation between  $\log \varrho$  and  $1/T$  is represented in fig. 4. Looking first at the right-hand part (room temperature and lower) we see that as the content of  $\text{ZnCr}_2\text{O}_4$  increases the curves gradually assume a

steeper slope, which means to say that the t.c. increases. Moreover, it is to be seen that at a certain temperature also the resistance increases with increasing  $\text{ZnCr}_2\text{O}_4$  content. This latter behaviour is easily understood, for with increasing  $\text{ZnCr}_2\text{O}_4$  content — according to our “rules” formulated above — the numbers of  $\text{Fe}^{2+}$ - and  $\text{Fe}^{3+}$ -ions (which continue to be mutually equal) decrease in the octahedral holes (see table I). Since, as we have seen, the presence of the “mixture” of these ions in the crystallographically equivalent sites is an essential condition for the low resistivity, the latter must therefore increase with the  $\text{ZnCr}_2\text{O}_4$  content.

Table I. Distribution of the metal ions among the available tetrahedral and octahedral holes in the mixed crystal  $\text{Fe}_3\text{O}_4\text{-ZnCr}_2\text{O}_4$  at various mixing ratios.

Mixing ratio $\text{ZnCr}_2\text{O}_4 : \text{Fe}_3\text{O}_4$	Tetrahedral holes		Octahedral holes		
	$\text{Zn}^{2+}$	$\text{Fe}^{3+}$	$\text{Cr}^{3+}$	$\text{Fe}^{2+}$	$\text{Fe}^{3+}$
1/4 : 3/4	1/4	3/4	1/2	3/4	3/4
1/2 : 1/2	1/2	1/2	1	1/2	1/2
3/4 : 1/4	3/4	1/4	3/2	1/4	1/4

The left-hand part of fig. 4, partly an extrapolation to  $T = \infty$ , shows a sudden bend in the curves for the highest  $\text{ZnCr}_2\text{O}_4$  content; we shall not go into an explanation of this here.

Since the slope of the  $\log \varrho\text{-}1/T$  curves determines the t.c., it is important to note that the “fan” of these curves may have a very different appearance according to the variety of spinels used as the non-conducting component of the mixed crystal. We will therefore go more closely into a second system, that of  $\text{Fe}_3\text{O}_4\text{-MgCr}_2\text{O}_4$ . Fig. 5 gives the  $\log \varrho\text{-}1/T$  curves for various compositions of this system. It is seen that close to the mixing ratio 1 : 1 there is a sudden increase in the slope of the curves, greater than the difference between neighbouring curves for other mixing ratios. The fan of curves is thereby clearly divided into two groups. The same appears also in fig. 6, where the “activation energy”  $\varepsilon$  — which according to equations (1), (3) and (4) is proportional to the slope of these curves — has been plotted as a function of the composition of the mixture both for the system  $\text{Fe}_3\text{O}_4\text{-MgCr}_2\text{O}_4$  and for the system  $\text{Fe}_3\text{O}_4\text{-ZnCr}_2\text{O}_4$ . Just before the mixing ratio 1 : 1 is reached the activation energy for the mixed crystal  $\text{Fe}_3\text{O}_4\text{-MgCr}_2\text{O}_4$  appears to rise suddenly, contrary to the case of  $\text{Fe}_3\text{O}_4\text{-ZnCr}_2\text{O}_4$ , where the activation energy increases very gradually with the  $\text{ZnCr}_2\text{O}_4$  percentage.

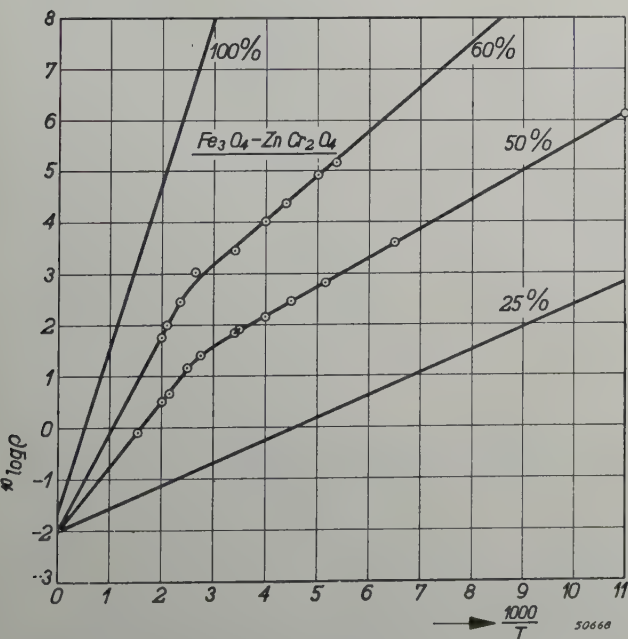


Fig. 4. Logarithm of the specific resistivity  $\sigma$  (in  $\Omega\text{ cm}$ ) as function of  $1/T$  ( $T$  absolute temperature) for the mixed crystal  $\text{Fe}_3\text{O}_4\text{-ZnCr}_2\text{O}_4$  for different percentages of  $\text{ZnCr}_2\text{O}_4$ .



This behaviour of the  $\text{Fe}_3\text{O}_4\text{-MgCr}_2\text{O}_4$  system may again be explained by means of our “rules” combined with what has been said above about the mechanism of conduction in  $\text{Fe}_3\text{O}_4$ . Contrary to the

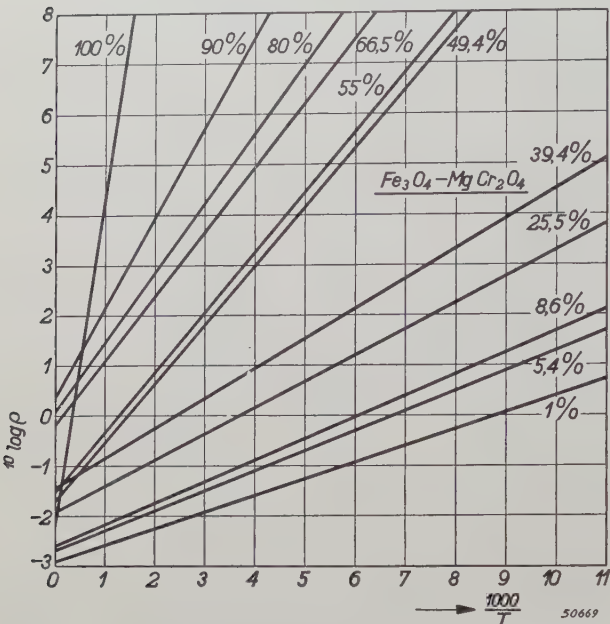


Fig. 5. Logarithm of the specific resistivity  $\sigma$  (in  $\Omega$  cm) as function of  $1/T$  ( $T$  absolute temperature) for the mixed crystal  $\text{Fe}_3\text{O}_4\text{-MgCr}_2\text{O}_4$  for different percentages of  $\text{MgCr}_2\text{O}_4$ .

case of  $\text{Fe}_3\text{O}_4\text{-ZnCr}_2\text{O}_4$ , where a certain number of  $\text{Fe}^{2+}$ - and  $\text{Fe}^{3+}$ -ions are found in the octahedral holes for any mixing ratio, here the number of  $\text{Fe}^{3+}$ -ions in the octahedral holes for a  $\text{MgCr}_2\text{O}_4$  content of 50% or higher is zero (see table II). The conduction mechanism which was so favourable for a low resistance can then no longer function and is apparently replaced by another less favourable mechanism; hence the jump observed in the activation energy.

Table II. Distribution of the metal ions among the available tetrahedral holes in the mixed crystal  $\text{Fe}_3\text{O}_4\text{-MgCr}_2\text{O}_4$  at various mixing ratios.

Mixing ratio $\text{MgCr}_2\text{O}_4 : \text{Fe}_3\text{O}_4$	Tetrahedral holes			Octahedral holes			
	$\text{Fe}^{3+}$	$\text{Fe}^{2+}$	$\text{Mg}^{2+}$	$\text{Mg}^{2+}$	$\text{Cr}^{3+}$	$\text{Fe}^{2+}$	$\text{Fe}^{3+}$
1/4 : 3/4	1	0	0	1/4	1/2	3/4	1/2
1/2 : 1/2	1	0	0	1/4	1	1/2	0
3/4 : 1/4	1/2	0	1/2	1/4	3/2	1/4	0
	1/2	1/4	1/4	1/2	3/2	0	0

For a content of  $\text{MgCr}_2\text{O}_4$  greater than 50% the distribution of the metal ions among the available holes is not unambiguously determined by our rules, as is evident also in table II. It is not impossible

that there may then be a “mixture” of  $\text{Fe}^{2+}$ - and  $\text{Fe}^{3+}$ -ions in the tetrahedral holes; the latter, however, will be farther apart, so that the situation will presumably indeed be less favourable for good conduction than in the case where the octahedral holes contain this mixture.

This abnormal behaviour of the  $\text{Fe}_3\text{O}_4\text{-MgCr}_2\text{O}_4$  system can be turned to good account if, for instance, a material is desired which has a specific resistivity of 100-1000  $\Omega$  cm at room temperature and at the same time a high t.c. for such a resistance value. Mixed crystals containing  $\text{MgCr}_2\text{O}_4$  satisfy this requirement much better than those with  $\text{ZnCr}_2\text{O}_4$ , since the resistance value quoted corresponds to a non-conducting spinel content of 50-60%, for which content the slope of the curves for mixed crystals with  $\text{MgCr}_2\text{O}_4$  is relatively great.

As regards the choice of  $\text{MgCr}_2\text{O}_4$  or  $\text{ZnCr}_2\text{O}_4$  as non-conducting spinel we would make the following observation. In order to regulate easily the resistivity of the mixed crystal it is desirable that the conductivity should originate exclusively from the presence of  $\text{Fe}^{2+}$ - and  $\text{Fe}^{3+}$ -ions in the crystal. Therefore in principle we should not use metals which, like iron, are apt to give ions of different valencies, such as Mn, Co, Ni, for then the conductivity might arise from the presence of, say,  $\text{Co}^{2+}$ - and  $\text{Co}^{3+}$ -ions, which is just what we want to avoid. From this point of view  $\text{MgAl}_2\text{O}_4$  is therefore the most suitable non-conducting spinel, because Mg and Al can only be bivalent and trivalent respectively. It appears, however, that a mixture of  $\text{MgAl}_2\text{O}_4$  and  $\text{Fe}_3\text{O}_4$  is difficult to sinter into a homogeneous phase. For

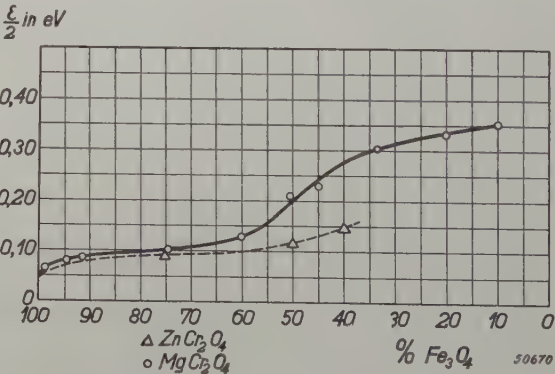


Fig. 6. The activation energy  $\varepsilon$  (in eV) as function of the percentage of  $\text{Fe}_3\text{O}_4$  for mixed crystals of  $\text{Fe}_3\text{O}_4\text{-ZnCr}_2\text{O}_4$  (broken line) and  $\text{Fe}_3\text{O}_4\text{-MgCr}_2\text{O}_4$  (fully-drawn line).

this reason we have used the more easily sintering chromites. Although chromium may occur in various valencies, under the experimental conditions in question we have not found any change in the valency of chromium in mixed crystals of  $\text{MgCr}_2\text{O}_4$  with  $\text{Fe}_3\text{O}_4$ .  $\text{Zn}_2\text{TiO}_4$  allows of a still lower sintering



temperature but the t.c. is not as high as with  $\text{MgCr}_2\text{O}_4$ .

#### *Stability and reproducibility of h.t.c. resistors*

The principle upon which h.t.c. resistors are based — producing semi-conductors with a certain specific resistivity and temperature coefficient by preparing mixed crystals of conductive  $\text{Fe}_3\text{O}_4$  and a non-conducting spinel — has various advantages over other already known means.

Resistors having the desired properties have previously been made from conducting and non-conducting grains homogeneously mixed and then sintered to a cohesive mass. As an example may be mentioned the mixture of Si powder and clay<sup>8)</sup>. With this mixture the resistivity is governed by the transitory resistance from one Si grain to the other. The number of contact points naturally depends upon the mixing ratio, the resistivity increasing with the concentration of clay. This kind of resistor has all sorts of drawbacks: the resistivity is extremely sensitive to small fluctuations in the mixing ratio and is difficult to reproduce; moreover, there is always the danger of the resistance mass not being sufficiently homogeneous, so that the current may easily concentrate along certain paths, which may even lead to short-circuiting due to local heating and resultant reduction of resistivity<sup>9)</sup>. Since silicon readily oxidizes in the atmosphere these resistors cannot be used without special precautions being taken.

A second method of making resistors suitable for the applications described is based upon the preparation of substances with a small deviation from the stoichiometric composition (cf. the article quoted in footnote<sup>1)</sup>). In this kind of substance the resistivity usually drops with increasing deviation from the stoichiometric composition, particularly as long as the deviation is still small. In the case of an oxidic material, for instance  $\text{NiO}$ , in order to get a certain deviation from the stoichiometric state in the direction of an excess of oxygen, the oxygen pressure and the temperature have to be very accurately adjusted in the preparation of the material. In practice this proves to be difficult and a reproducible adjustment to a certain resistivity is faced with insurmountable obstacles. Furthermore the slightest change in the oxygen content of the

material during use will result in a relatively large change in the resistivity.

The question now arises whether the deviation from the stoichiometric state in the resistors made with  $\text{Fe}_3\text{O}_4$  as basic component may not lead to difficulties.  $\text{Fe}_3\text{O}_4$ , too, can be prepared with a certain deviation from the stoichiometric state. In particular it is possible to get a deviation in the direction of an excess of oxygen. It is even possible to prepare any composition between  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$ . All these substances are homogeneous and have the spinel structure. The relative excess of oxygen, compared with  $\text{Fe}_3\text{O}_4$ , is obtained because the lattice contains too few  $\text{Fe}^{2+}$ -ions. The limiting case,  $\text{Fe}_2\text{O}_3$  (the so-called  $\gamma$ -modification of ferric oxide) should therefore really be written in our notations as  $\text{Fe}^{3+}(\text{Fe}_{1.67}^{3+})\text{O}_4$ . The intermediate cases can be regarded as mixed crystals of  $\text{Fe}_3\text{O}_4$  and  $\gamma\text{-Fe}_2\text{O}_3$ . All these mixed crystals, however, can only be prepared by some artifice or other and they are not stable; only those containing little  $\text{Fe}_2\text{O}_3$ , less than 10 %, can be prepared in the usual way by heating ferric oxide directly in an atmosphere containing more or less oxygen.

It is to be expected that the resistivity of these mixed crystals will increase with the  $\text{Fe}_2\text{O}_3$  content, for according to our "rules" the higher the  $\text{Fe}_2\text{O}_3$  content the fewer will be the number of  $\text{Fe}^{2+}$ -ions in the octahedral holes. And, if our explanation of the good conductivity in  $\text{Fe}_3\text{O}_4$  is correct, this should be manifested in an increase of the specific resistivity. It is known that  $\gamma\text{-Fe}_2\text{O}_3$  is almost an insulator. The values found for the specific resistivity of  $\gamma\text{-Fe}_2\text{O}_3$  however are not all reproducible, firstly because this material cannot be sintered, so that measurements have to be taken with the powder, and secondly because traces of  $\text{Fe}^{2+}$ -ions considerably reduce the resistivity; the situation here is thus comparable to the abovementioned case of  $\text{NiO}$ , which also becomes conductive through small deviations from the stoichiometric state. With 100%  $\text{Fe}_3\text{O}_4$  on the other hand we find that small deviations from the stoichiometric state cause but little change in the specific resistivity.

This insensitivity of  $\text{Fe}_3\text{O}_4$  to small deviations from the stoichiometric composition usually prevails also in mixed crystals of  $\text{Fe}_3\text{O}_4$  with non-conducting spinels. If, therefore, the sintering temperature, the oxygen content of the atmosphere and the duration of heating are so chosen that the mixed crystal has approximately the spinel composition, then any small variation in the process of manufacture will have little effect upon the resistivity. This explains for a large part the constancy and

<sup>8)</sup> These so-called "Starto" resistors have been dealt with in this journal (Philips Techn. Rev. 1, 205-210, 1936).

<sup>9)</sup> Of course such difficulties may arise with all inhomogeneous resistors, so that it is quite evident that there is an advantage in using mixed crystals, these being homogeneous.



also the great stability of the electrical properties of h.t.c. resistors. As a matter of fact the composition itself is quite stable: the densely sintered materials show relatively little reaction; moreover, the reactivity of  $\text{Fe}_3\text{O}_4$  towards oxygen seems to be retarded by the presence of the other spinel. Consequently in many applications where the ambient temperature is low enough or the load sufficiently weak for the temperature not to rise above a few hundred degrees Centigrade, these h.t.c. resistors

can be used without any screening. (At higher temperatures they have to be used in a protective gas, e.g. nitrogen, or in a vacuum.) When it is considered, moreover, that any desired resistivity of the h.t.c. resistors can easily be obtained by a suitable choice of the mixing ratio of  $\text{Fe}_3\text{O}_4$  and a non-conducting spinel in the mixed crystal, the great advantages that these new materials possess over those hitherto used will be still more apparent.

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# THE DRYING LAMP AND ITS MOST IMPORTANT APPLICATIONS

by Th. J. J. A. MANDERS.

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Nowadays electric drying-lamps are being used for numerous drying processes in industry. These lamps are electric sources of infra-red of the incandescent type specially designed for the purpose. In this article first some properties of infra-red rays are brought to mind, it then being shown how infra-red rays are absorbed in a layer of water and how they then behave with respect to lacquers. The conditions are considered which have to be satisfied by a drying lamp. In the designing of the Philips drying lamp it has been endeavoured to make this lamp answer the requirements as closely as possible. All sorts of factories have already been equipped with large numbers of drying lamps for drying semi-manufactured goods and final products. Among the many possibilities offered by this lamp the drying of lacquers and of textiles and paper is particularly discussed.

## Introduction

Drying is a process applied in many industries. Investigations into the best methods of production have in many cases recently led to a conversion from the old drying methods (*e.g.* with a coal-fired oven) to the use of drying lamps. These are electric infra-red sources specially designed for the purpose.

The object of drying is usually to cause water or some other liquid to evaporate. In some cases this is attended by a chemical conversion, for instance oxidation in the hardening of enamels and polymerisation in the drying of synthetic lacquers.

As a rule a drying process is speeded up by heating. This heating is a question of the transmission of heat, and as is known this transmission can be brought about in three ways, by:

- a) conduction,
- b) convection,
- c) radiation.

In the drying methods used in industry conduction plays a minor part. By convection heat is transferred from the source to the object to be heated through a medium (a liquid or a gas). The heat transfer coefficient between air and metal is low and between air and lacquer still lower. The heat then has to penetrate deeper into the object through conduction. The heat conduction coefficient of most substances that have to be dried is likewise low. In heating through convection these are two adverse factors which do not arise in the case of radiation, for in the latter case the heat is transferred entirely without the aid of a medium. It is for this reason that the method of radiation usually yields the best results. Under properly balanced working the energy is absorbed in the different layers of the object and at the same time evenly converted into heat down to a certain depth. In the layers in which this takes place the temperature rises rapidly and uniformly. This ac-

counts for the fact that drying by radiation as a rule takes much less time than is the case by convection.

With the drying lamp the heat transfer takes place for the greater part through infra-red radiation. It is therefore advisable, before dealing with our subject proper, to give a brief account of some of the properties of infra-red radiation, as we shall have to refer to these when discussing this lamp and its applications.

## The properties of infra-red radiation

The wavelength of infra-red rays is longer than that of red light. The boundary between visible and invisible radiation lies at about 7600 Å. Infra-red radiation of a wavelength of  $4.2 \times 10^6$  Å has, however, also been observed. Light waves are often compared with sound waves, and if we do so here we may say that visible light covers one octave and infra-red radiation nine octaves.

To judge the nature of the radiation of a solid body a graph may be drawn of the energy emitted as a function of the wavelength. It will then be seen that for any temperature of the body the spectral emission curve has a maximum for one certain wavelength.

In *fig. 1* spectral emission curves are given for a black body radiator with a temperature of 6000 °K, for a photo lamp ("Photolita"), a normal incandescent lamp ("Bi-Arlita") and the drying lamp discussed in this article. For a temperature of 6000 °K the maximum of the emission lies at a wavelength of 4800 Å. In the case of the "Photolita" lamp the filament temperature is 3400 °K and  $\lambda_{\max} = 8150$  Å, whilst these figures for the 100 W "Bi-Arlita" lamp are 2850 °K and 9500 Å. The temperature of the tungsten coil in the drying lamp is 2200 °K and the wavelength of the maximum emission is 12 000 Å.

For black body radiation there is a simple relation



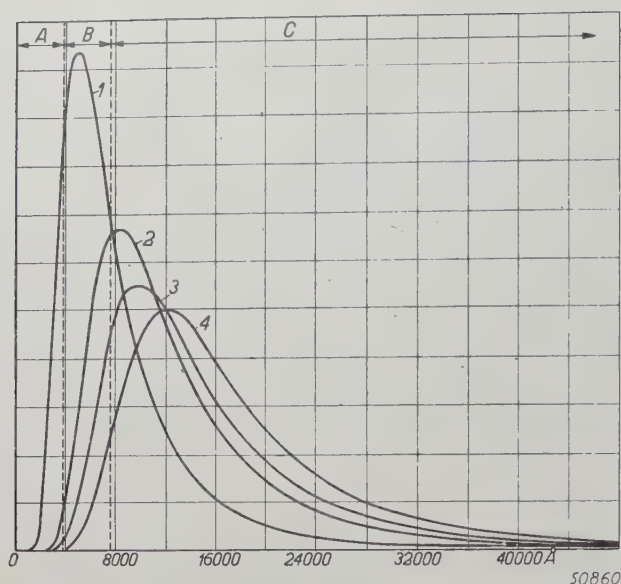


Fig. 1. Relative spectral energy distribution for some radiators at an equal quantity of total energy emitted:

- 1) for a black body at a temperature of 6000 °K;
  - 2) for the coil of a "Photolita" lamp (temperature 3400 °K);
  - 3) for the coil of a 100 W "Bi-Arlita" lamp (2850 °K);
  - 4) for the 250 W drying lamp with a temperature of 2200 °K.
- A is the range of ultra-violet radiation, B that of visible light and C that of infra-red radiation.

between the absolute temperature  $T$  of the incandescent body and the wavelength of the maximum emission. This is Wien's displacement law:

$$\lambda_{\max} T = 288 \cdot 10^5,$$

where  $\lambda_{\max}$  is expressed in Angström and  $T$  in degrees Kelvin. Since all known incandescent bodies differ more or less from a black body radiator, their displacement laws differ from Wien's. According to Geiss, the displacement law for a disc of tungsten in the temperature range from 2200 to 3400 °K is <sup>1)</sup>:

$$\lambda_{\max} T = 263 \cdot 10^5 + (T - 2500) \cdot 10^3$$

and for a coiled tungsten wire, where the radiation

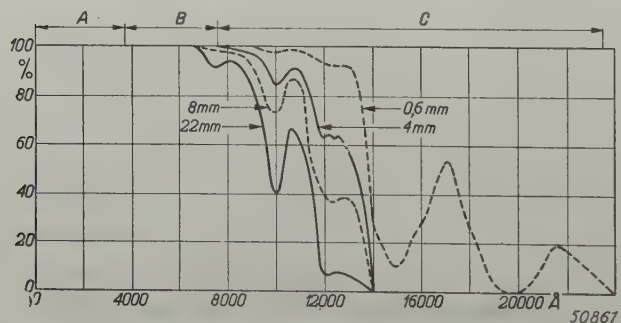


Fig. 2. The transmission of infra-red rays of different wavelengths through layers of water of different thickness. It appears that the layers of 22, 8 and 4 mm thickness absorb all energy of wavelengths above 14 000 Å.

<sup>1)</sup> W. Geiss, Trocknen mit infraroten Strahlen, Electrical Service 20, 287-293, 1945/46.

from the part between the windings of the coil may be regarded as being practically black, for the same interval:

$$\lambda_{\max} T = 268 \cdot 10^5 + (T - 2500) \cdot 10^3.$$

With the help of this equation it is possible to design a lamp having a certain value for the wavelength of its maximum emission.

Since the evaporation of water is an important task of the drying lamp it is worth while investigating what happens when infra-red rays are directed upon a layer of water.

Water readily lets visible light pass through it but not so infra-red rays. Investigations with shallow depths of water have shown that the most important absorption bands in the infra-red part of the spectrum lie in the wavelengths of 15 000, 20 000, 30 000, 47 500 and 60 000 Å. Fig. 2 gives a graphic representation of the transmission factor of infra-red radiation of different wavelengths through lay-

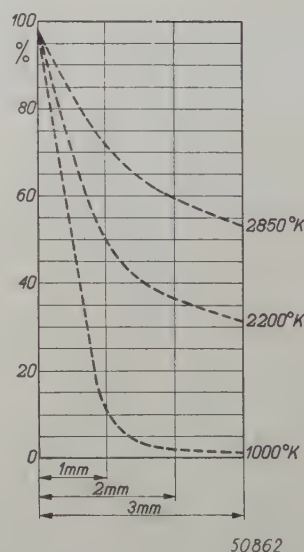


Fig. 3. Transmission of the energy emitted by three different infra-red sources (normal incandescent lamp, drying lamp, heating element of 1000 °K) through successive depths of water. Of the radiation from a drying lamp 50%, 13% and 5% is absorbed in the first, second and third millimeter respectively.

ers of water of different thickness. It is to be seen that the radiation with wavelengths above 14 000 Å is practically entirely absorbed by the layer of water unless the latter has very little thickness, viz. less than 0.5 mm.

Fig. 1, however, shows that the lamps commonly used radiate a continuous spectrum, thus emitting energy of quite different wavelengths. It is therefore worth investigating at what depths of water the rays emitted from various infra-red sources are mainly absorbed. The graphs in fig. 3 indicate the

transmission as a function of the thickness of the layer when irradiating with a heating element (temperature 1000 °K), a tungsten filament lamp (2850 °K) and the Philips drying lamp (2200 °K).

Drying lamps are also being widely used for the drying of lacquers, and we therefore also have to find out how infra-red rays behave towards the most commonly used kinds of lacquers. This is shown in

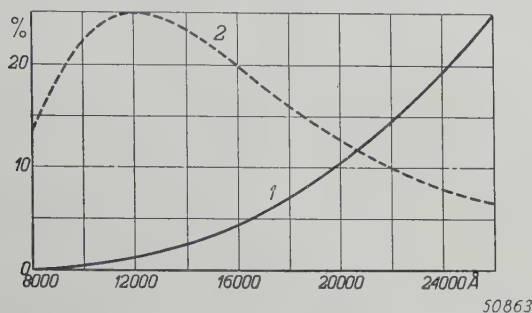


Fig. 4. Transmission of infra-red rays when drying lamps are used for lacquers. Curve 1 gives an idea of the transmission of a certain kind of lacquer for infra-red energy of different wavelengths. For comparison curve 2 gives the spectral energy distribution of the Philips drying lamp.

fig. 4, where curve 1 gives an idea of the transmission of infra-red energy through lacquers as a function of the wavelength. It is to be borne in mind, however, that the shape of this curve depends upon the thickness of the layer and the kind of lacquer. It appears that with lacquers the infra-red energy with a wavelength  $< 14\,000\text{ Å}$  is almost entirely absorbed, but if a longer wavelength is used the amount of energy allowed to pass through increases. By way of comparison the spectral energy distribution of the Philips drying lamp is also drawn in the same diagram (curve 2).

Having now considered the behaviour and properties of infra-red radiation, it is possible to indicate how a drying lamp can best be constructed.

#### The requirement to be fulfilled by a drying lamp

When one is about to design a drying lamp the first question to be considered is what the wavelength of the maximum emission is to be. We have seen that this depends upon the absolute temperature of the filament of the lamp.

It is of primary importance that the radiation should be converted into heat in the object to be dried as completely as possible and in exactly the right place. If the absorption takes place only on the surface it means that the underlying layers have to be heated through conduction. Since most substances that have to be dried are bad heat conductors this is not desirable. With lacquers we have the further difficulty that if the surface is

dried too intensively the skin becomes tough while the underlying layers are still soft. On the other hand too high a transmission means that energy will be lost or the sub-layers heated too much. It is therefore a matter of great importance to balance carefully the ratio of absorption to transmission. The ideal solution is to have sufficient energy penetrating close down to the sub-layer, so that the whole of the layer to be dried absorbs the radiation while the sub-layer is moderately heated.

When the drying lamp has to be used for evaporating water we can deduce from fig. 2 the wavelength required for the maximum emission and thus also the temperature of the lamp filament. The graph shows that the energy of infra-red rays having wavelengths longer than  $14\,000\text{ Å}$  is practically entirely absorbed in the top layer, except in the case of a very thin layer of water, e.g.  $< 1\text{ mm}$ . Therefore, to ensure that the rays penetrate deep enough into the layer of water,  $\lambda_{\text{max}}$  should be chosen lower, but the wavelength may not be so short that too much radiation is allowed to pass through.

From fig. 3 it is to be seen that a radiator with a temperature of say 2850 °K would not be suitable for our purpose, because the water would allow too much of the energy to pass through it <sup>2)</sup>.

A second objection attaching to such a high temperature is the unfavourable effect it has upon the life of the lamp, which must be economically justified.

A  $\lambda_{\text{max}}$  of  $12\,000\text{ Å}$  appears to be a good choice for evaporating water. The filament temperature corresponding to this wavelength is 2200 °K. Fig 3 shows to what extent the energy from such a lamp is absorbed in the successive layers. The first millimeter of water absorbs 50%, the second 13% and the third 5%.

Now that we have seen what is the most suitable filament temperature for evaporating water, the next question to be considered is how a radiator should be constructed for the drying of lacquers. Fig. 4 supplies the answer. It is seen that the top of the distribution curve should anyhow lie below  $15\,000\text{ Å}$ , because otherwise the transmission would be too high. If this condition is satisfied it appears further that for this purpose the value of  $\lambda_{\text{max}}$  is not very critical. Closer investigation has shown that it makes practically no difference in the drying time whether  $\lambda_{\text{max}}$  is  $12\,000\text{ Å}$  or slightly lower or

<sup>2)</sup> It is in connection with this that the "Infraphil", an apparatus for medical therapy with infra-red rays, is fitted with a lamp that has a filament temperature of 2800 °K. The radiation from this lamp has to penetrate the water-containing epidermis to impart heat to the underlying tissues. See Philips Techn. Rev. 8, 177-182, 1946 (No. 6).



higher. Apparently, therefore, the same lamp can be used for lacquers as for water.

Now that we have found the optimum wavelength for the maximum emission we shall consider the further requirements that the source of radiation has to satisfy.

The temperature found is so high as to make it necessary to envelop the filament in a glass bulb. In order to reduce evaporation this bulb has to be filled with an inert gas, just as is the case with normal incandescent lamps. Further, the lamp should be constructed in such a way that the largest possible part of the radiation is directed upon the object to be dried. The part of the radiation that is not emitted in the desired direction must therefore be reflected. In the construction of a reflector, however, it must be taken into account that the reflection coefficient of different materials depends upon the wavelength of the radiation. Fig. 5 gives a general

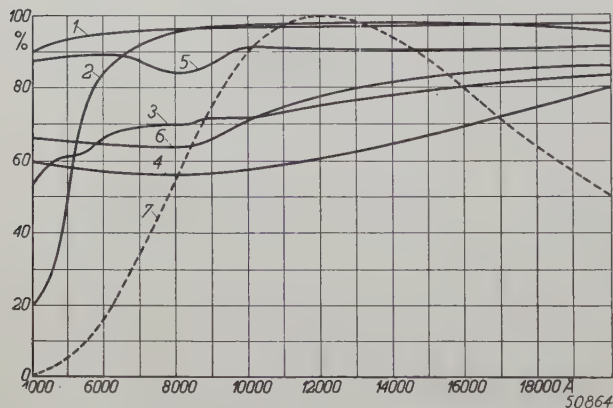


Fig. 5. The reflection coefficient, expressed as a percentage of the incident energy, of some metals that could be used as mirror of a drying lamp, 1 is silver, 2 gold, 3 nickel, 4 chromium, 5 evaporated aluminium and 6 polished aluminium. For comparison curve 7 gives the spectral energy distribution of the radiator.

idea of the reflection coefficients of some suitable materials for visible light and for the most important part of the infra-red radiation (7600 up to 20 000 Å). It appears that within the range in question silver has a great reflectivity (92-98%), as is also the case with gold (84-98%), whilst nickel (65-80%) and chromium (58-70%) are less suitable. These graphs also show that evaporated aluminium (unlike polished aluminium) is an exceptionally good reflector.

The choice between silver, gold and aluminium as material for the reflector depends also upon the question whether the mirror is to be applied inside the bulb or outside. In America an external reflector is very much used. When an external reflector is applied in the drying, for instance, of lacquers usually a gold mirror is recommended because of the

influence of the lacquer vapours upon the reflector. In Europe an internal reflector is most commonly used, because of the following advantages:

- 1) it retains its high reflection coefficient much better than an external reflector, because it is not subject to chemical or mechanical influences and is free from dust;
- 2) it takes up less space and requires no special means of attachment;
- 3) the whole radiation passes through the wall of the bulb only once. This means less absorption in the glass wall; in the case of an external reflector part of the radiation passes through the wall of the bulb three times.

For a radiator with an internal reflector gold, silver and aluminium vaporised in vacuum are all equally useful as regards reflection. Since gold, however, is expensive and silver is in this case less satisfactory from the point of view of manufacture, aluminium is used. The aluminium is evaporated and condensed on the inside of the glass bulb.

For a proper bundling of the rays it is advisable to shape the reflector like a paraboloid and to place the radiating body as far as possible in its focus.

If the rays pass through only once the question of absorption in the glass wall is not very important. A graph of the transmission factor of normal calcium glass of a thickness of 1 mm for various wavelengths <sup>3)</sup> shows that appreciable absorption begins at a wavelength of 25 000 Å. Within the range that counts most for our purpose the transmission of normal glass is good.

### Properties of the Philips drying lamp

We will now give a brief description of the latest type of Philips drying lamp. On account of the considerations mentioned above and also on specifically lamp-technical grounds which cannot be analysed here, this lamp has been given a shape as outlined in fig. 6 and shown in the photograph in fig. 7. The glass bulb has a parabolic part and a spherical widening at the level of the filament.

The incandescent body is a tungsten coil which takes up 250 W. The temperature of 2200 °K determines — as already remarked — also the life of the lamp. The life of an ordinary incandescent lamp (for instance the 100 W "Bi-Arlita", temperature 2850 °K) is 1000 burning hours, whereas that of the Philips drying lamp is 5000. The bottom of the bulb is relatively strongly convex, giving it a robust form. To get a uniform irradiation the wall of the bulb is slightly satin-frosted and the incandescent

<sup>3)</sup> Philips Techn. Rev. 8, 180, 1946 (No. 6).



element is of the smallest possible dimensions. This drying lamp may be provided with either a screw cap or a bayonet cap. At temperatures above 200 °C the usual method of cementing the lamp in the cap

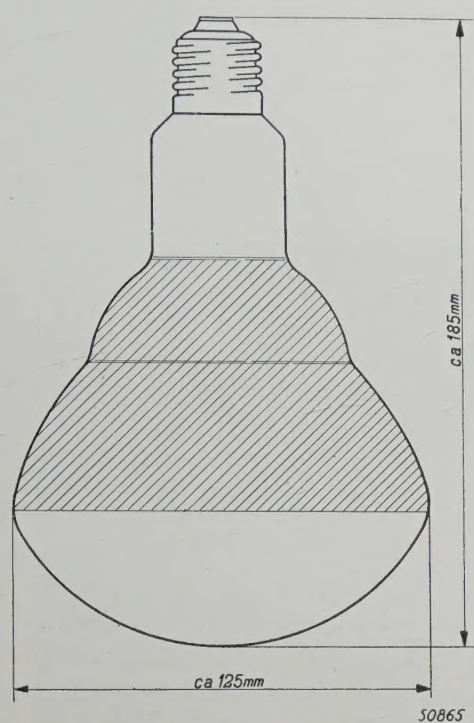


Fig. 6. Dimensions and shape of a Philips drying lamp.

is not reliable and for that reason a lamp base has been developed which allows of this joint being made without the use of cement.

With the aid of a thermopile the intensity of radiation has been measured at various points of planes perpendicular to the axis of the lamp, the planes being at distances of 10 to 100 cm away from the front of the lamp. Table I gives the results of these measurements expressed in mW/cm². As a compa-

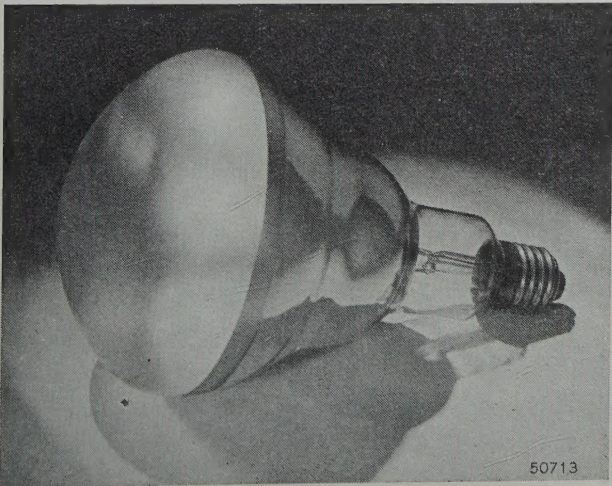


Fig. 7. The 250 W Philips drying lamp.

ris on, the radiation intensity of the sun at its zenith under favourable conditions is 100 mW/cm². Fig. 8 gives a graph of the distribution of radiation intensities. The table and the graph show there is uniform radiation intensity on planes 20-60 cm away from the bottom of the bulb within a cone having an apex angle of 30 degrees. With the aid of these data it is possible to determine the optimum arrangement of a number of drying lamps in relation one to the other and to the object.

It will seldom occur that only one drying lamp is used for a certain purpose. In industries it is usual to work with a drying plant containing a number of lamps.

- The drying time depends upon various factors:
- a) the nature of the substance to be dried,
  - b) the nature of the sub-surface (its thickness and heat conductivity),
  - c) the distance between the lamps and the object and the number of lamps used, or in other words the energy supplied per cm².

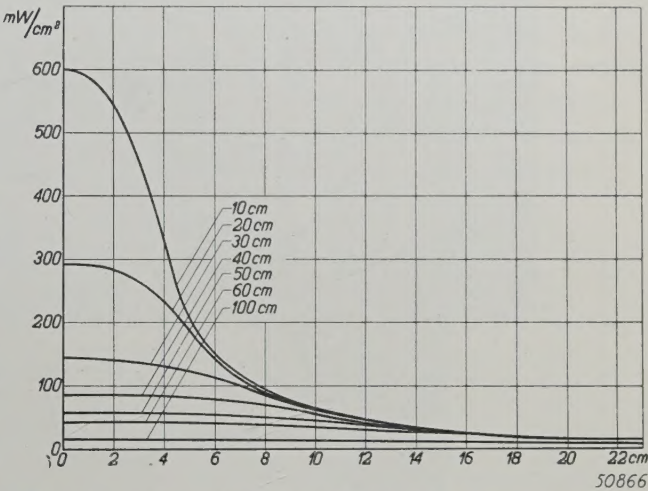


Fig. 8. Graphic representation of the distribution of the radiation intensities (in mW/cm²) in planes perpendicular to the lamp axis at different distances away from the lamp varying from 10 to 100 cm. The horizontal axis gives the distance between the point in question and the lamp axis.

Table I. Radiation intensity at different distances from the lamp expressed in mW/cm². The distance from the front of the lamp to the plane of measurement (in cm) is represented by *h* and the distance from the point of measurement to the axis of the lamp (in cm) by *r*.

<i>h</i> \ <i>r</i>	0	2½	5	10	15	20	30	40	50	60
10	600	500	250	65	32	19	10	5	3	2
20	290	275	190	65	31	19	10	5	3	2
30	145	140	125	65	30	18	10	5	3	2
40	85	85	80	56	29	18	9	5	3	2
50	56	56	53	43	26	17	9	5	3	2
60	42	42	40	33	23	15	9	5	3	2
100	14	14	14	14	13	12	9	5	3	2



In factories the objects to be dried are usually placed on a conveyor belt which passes through a tunnel in which a number of lamps are mounted in such a way that their beams are directed upon the belt. The number of lamps, the distances away from the object and the speed of the conveyor belt should be so chosen that the drying is completed by the time the object(s) have reached the end of the tunnel, taking into account the maximum temperature permissible for the object(s) to be dried.

The most important kinds of lacquers have an oil, synthetic or cellulose base. The drying and hardening processes of each of these kinds are based on different principles. In all three cases, it is true, the solvent has to be evaporated, but oil-base lacquers harden through oxidation of the binder (the oil), whilst in the case of synthetic-base lacquers (so named because they contain synthetic resins) although the binder is also hardened to a certain extent through oxidation it takes place

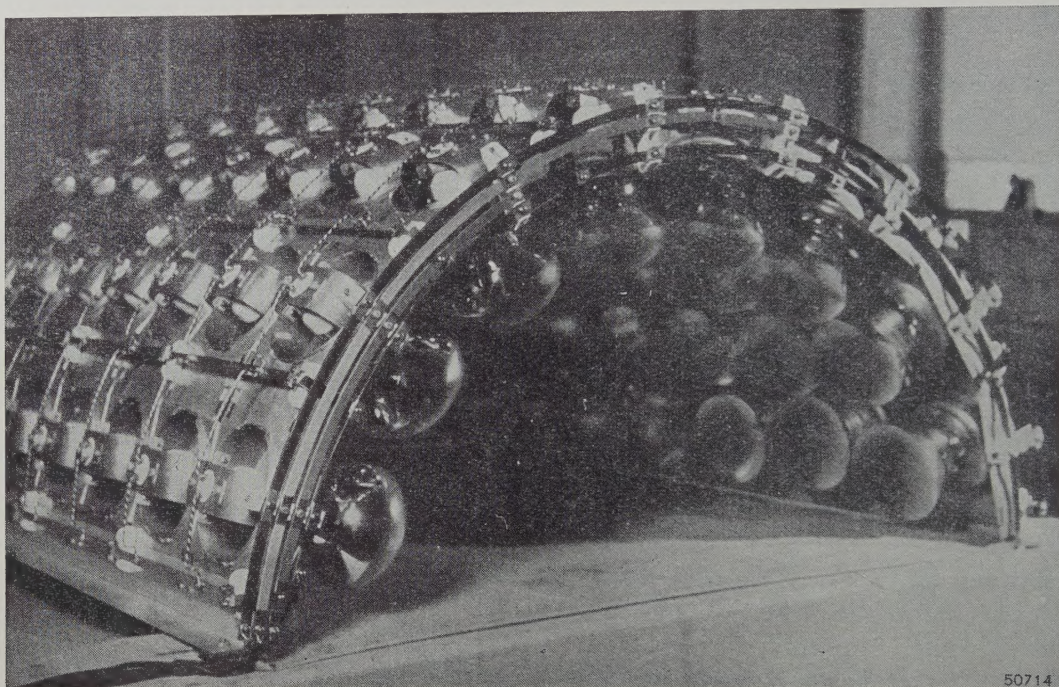


Fig. 9. A drying tunnel with Philips drying lamps, built up from "building elements" each containing one drying lamp.

Fig. 9 shows such a drying tunnel.

Such an installation can be built up from building elements consisting of the actual assembly unit and a lampholder (see fig. 9). These building elements can be combined in a simple manner to form larger units in flat or curved planes, an example of which is given in fig. 10.

## Applications

### *The drying of lacquers*

The drying of lacquered objects is an important application of drying lamps.

Lacquers contain a non-volatile binding agent and a volatile solvent. Furthermore most lacquers contain a pigment, generally an anorganic compound that does not dissolve but whose particles are mixed in the lacquer and give it a certain colour.

mainly through polymerisation. In the case of cellulose-base lacquers it is only a matter of evaporating the solvent.

Both the evaporating of the solvent and the oxidising or polymerising of the binder are processes which can be accelerated by raising the temperature, though only to within certain limits, because too rapid vaporisation causes blisters in the lacquer surface and too high temperatures may also change the colour.

According to the temperature at which the drying takes place, lacquers can be divided into those which dry in the atmosphere, those which dry fairly well already at room temperature, and baking enamels which only dry at a certain temperature. For the last mentioned category the drying process has to take place between that specific temperature and the maximum temperature permissible for the ob-



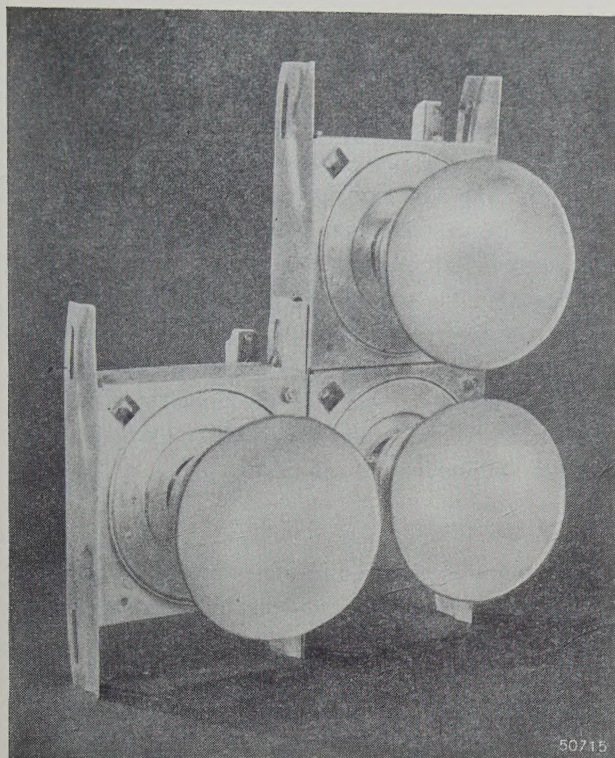


Fig. 10. Combination of three building elements (new type) each fitted with a drying lamp.

ject. It is recommendable that the temperature actually applied approaches the maximum as near as possible. Experiments have shown that during

the drying process the temperature of the layer of lacquer remains fairly constant. Baking enamels of an alkyd-resin base of different colours have the same hardness after 10 minutes irradiation as after 60 minutes processing in a baking oven. This opens great possibilities for increasing production or for the saving of space.

One of the first manufacturing firms in America to apply drying lamps on a large scale was the Ford Motor Co. They use drying lamps for drying lacquered motorcar bodies, which was formerly done with steam. *Fig. 11* shows a drying tunnel installed by the Ford Motor Co. at Detroit for car bodies carried through it continuously on a conveyor.

About 1939 the Ford factories were already using some 35 000 drying lamps. For the drying of the ground lacquer an oven is used, built in two halves placed around the car body suspended from a conveyor. The oven moves along with the conveyor for 7 minutes, after which time the ground lacquer is dry, whereas formerly this took 30 minutes. The drying time of the top coat has even been reduced from 80 to 14 minutes.

Apart from motorcar factories drying lamps are nowadays being very widely used in numbers of other industries where the drying of lacquers plays an important part (e.g. in aircraft factories).

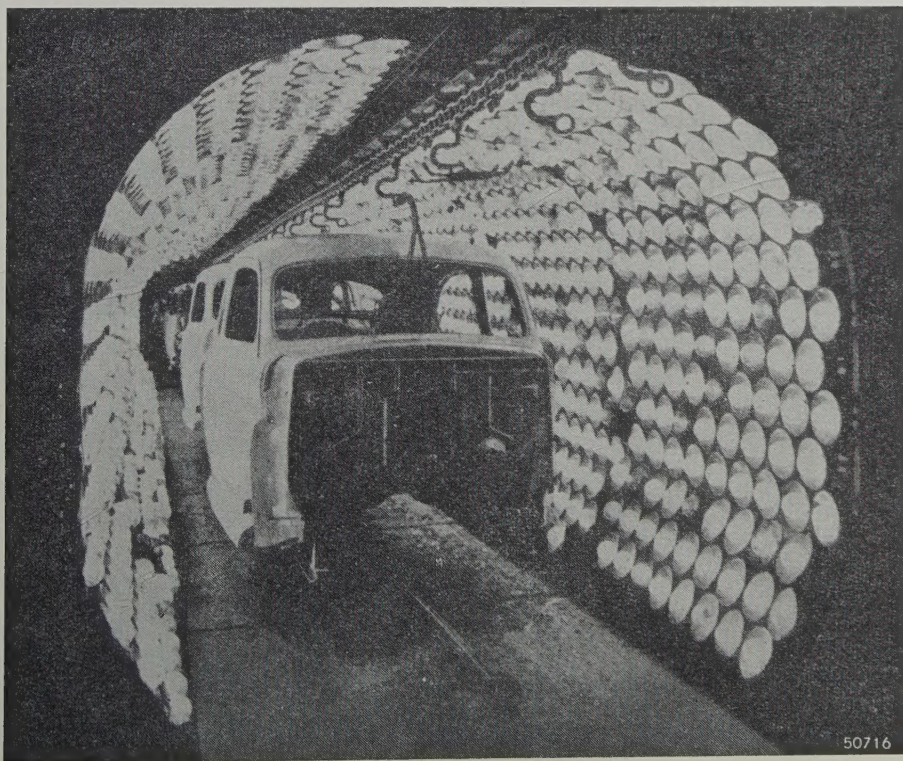


Fig. 11. A drying tunnel as used by the Ford Motor Co. at Detroit, where car bodies are passed through suspended from a conveyor.



### *The drying of textiles and paper*

In the textile and paper-making industries drying lamps are used to evaporate superfluous water from semi-manufactured goods or the finished products.

The "Vezelinstituut" at Delft, a laboratory for testing textile yarns, have conducted a series of experiments in order to find out in how far the drying of textiles by means of drying lamps had an adverse effect upon the breaking strength, the elongation upon fracture and the tint of dyed and undyed woollen, cotton, linen and rayon fabrics. As a result of a large number of practical tests it was established that irradiation with drying lamps has no adverse effect whatever upon these properties of those four materials. Further it was investigated how fabrics can be most economically dried with the aid of drying lamps.

Drying lamps are now being used in several textile mills. To mention an example: in one factory the yarns wound on spools used to be dried in an oven for anything from 4 to 16 hours, 45 kg being dried in 4 hours, during which time 7% of moisture was extracted. Now the yarns are rewound at a rate of 27.5 m/min. and passed through in a broad band side by side underneath a wall of drying lamps having a total capacity of 11 kW. Underneath the yarns is a reflecting plate which throws back onto the yarns the rays that have passed through. In this manner it is possible to dry in 1 hour the same quantity of yarns as it used to take 4 hours to dry.

Drying lamps are also being applied with great success in paper making, as may be illustrated by two examples.

When the temperature of the paper track is raised to 55-75 °C immediately before the last stage of wet pressing the viscosity of the water is reduced

and thus the water can be more easily pressed out. This has been known for a long time but it was very difficult to bring about this increase of temperature in a practicable manner. Drying lamps afforded an excellent solution. It was found that with these lamps and under the same compression 25-36% more water could be pressed out of the paper, which means a considerable increase in efficiency.

In another factory the after-drying of the paper used to be done with electric resistance elements, the plant having a capacity of 18.5 kW. After drying lamps had been installed a capacity of 4.2 kW was found sufficient for the same drying time, thus giving a saving in current of 75%.

### *Other possibilities*

Drying lamps are used in many other fields, as for instance for the drying of leather in tanneries and in boot and shoe factories, for the drying of tobacco and also of developed films.

One important application may be that of grass drying, which is still in an experimental stage. If it comes to be applied on a large scale it will mean a revolution in agriculture, for whereas there can only be one or two hay crops in a season young grass can be mown and dried five to seven times. Preliminary experiments have shown that drying lamp installations give about the same yield as drying machines fired with coke. When drying lamps are used, however, the product is of a better quality and, moreover, the cost of the plant is estimated to be much lower.

Drying lamps have also been used for drying vegetables and preserving fruit.

The future will undoubtedly reveal many more fields of application for these drying lamps.

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